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ARTICLE III.

SMELTING PROCESSES AT FREIBERG.

BY PERSIFOR FRAZER, JR.

Read June 17th, 1870.

THE present chart and text form part of a work intended to accompany an application for examination in Metallurgy at Freiberg, Saxony. The text follows the order of a preliminary course of lectures on the Freiberg Smelting Works, delivered at the works themselves, every day during the month of August, by Herrn Hütten—Assistant Marhold, and illustrated by personally examining the things spoken of. The plan of the chart is entirely original, and its execution may be said to be a crude and imperfect attempt to portray what actually takes place at the Smelting Works; and, while exhibiting the mutual relations of the different processes, so to separate them from each other, that they and the constituents entering into every one of them may be traced to their origins and applications. To do this it was necessary to condense the area of the chart as much as possible in order to allow the whole to be seen at a glance, and on the other hand some new symbolical method was requisite which should better conform in system to the real sequence of operations. The former plan, adopted by Lorenz and others in the “trees,” &c., seems to have several objections. In the first place, it takes up a much larger space, and renders it more difficult to get a general view of the whole cycle. Then, it permits only imperfectly the processes to be followed backwards (synthetically or from educts and products to ores and reagents), because these educts and products being separated and scattered over the whole text of the “tree,” are not so readily found, and when found must be traced back through six or seven disconnected descriptions of different substances advancing in complexity of chemical composition. The products of any particular process are, by this plan, necessarily strung out in horizontal

lines across a broad sheet, while the vertical lines represent more or less the advance of the substance either from simple to complex (synthetical—educt to ore) or complex to simple (analytical—ore to educt). This is the principle involved in this order of arrangement, but we shall see that it is but partially realized in fact.

This tree commences by describing in two long lines the kinds of ore brought to the lead process, which it makes the inception of all other processes.*

A long horizontal line is made to extend over the several products which result from this lead process, viz.: Lead slag—Raw lead—Lead Matt—Lead Speiss—Furnace ends—Furnace fume—Dust.

The Lead Matt is here considered the important product, and an arrow from this, points downward to the next horizontal line, which includes six products, and takes up as much space as the one above for the lead process. This second line cuts off any direct connection between any other of the seven products of the lead process, and the processes by which it is further treated. As this is repeated about twelve times, it will be apparent that the relations of these substances and processes to, and their dependence upon each other, far from being revealed, are effectually concealed; different substances which belong to the same process being so scattered over the whole sheet as to make a comprehensive view of that process impossible, and the fact that the same substance under different circumstances is treated differently, being only conveyed to the mind by two or three lines of text under the name of the substance.

Thus there are eleven products which, according to Lorenz, are treated in the Lead Matt Process, but those eleven names are so scattered on the sheet from the first line to the last, and from the right to the left, that it would be as easy to see at a glance the philological relations to each other of the words in a Worcester's Dictionary as those of these products.

It has been remarked that Lorenz's plan permits one to follow the processes synthetically, but this is the case only so far as it permits one to follow the *main line* from the educt or product through a *principal* product which has been used in each process up to the ore in which the educt or product was originally contained. What other materials have assisted in the process, and whether any other process may not have given the same product, you are not able to discover. For instance, if it is required to trace the course of raw lead from any particular process, it must be known beforehand where the previous product comes from. To know this, you must know how that product is found, and so on to the end. In other words, you must know exactly what you want to find out. It is

* It should be remarked that this other system does not pretend to deal with the auxiliary operations, such as sulphuric acid manufacture, zinc production, &c.

true that you can follow any product on which you happen to alight, and find out one line of main products through which the ore has been transformed to that particular one, but to understand even what other agencies have had their influence in the formation of the substance, you must consult either the text of the chart (in the few cases where such explanation is given) or some more detailed work on the Freiberg processes; and in addition to this defect it is not always easy when practically the same substance (as Raw Lead, &c.), resulting from different operations, is scattered in a dozen places on the "tree" to find that which is required. Again, it is not easy to follow the processes *analytically* as in their actual sequence, for the reason indicated before, that but one of the many products is selected as the most important in every line, and these lines separate one set of products from the others with which they are mixed for their further treatment. Another objection to it is, that it only mentions the composition of the charges in the most important cases, and leaves those reagents which are not ores, entirely out of consideration; and another, that no other but pyro-chemical processes are given, and not all of these. In the substitute which I propose for this "tree," the attempt has been made to attain to a system which, while it represents the actual sequence and co-sequence of processes, permits an empirical view of these which it requires but little technical information to understand.

SMELTING PROCESSES AT FREIBERG.

The Freiberg smelting processes have for their object the production of silver, lead, and copper (chiefly as blue vitriol), from the ores obtained from the royal Saxon mines; but, outside of these, from other purchased materials and foreign ores (as for example, jewelers' sweepings and American ores), and middle products from previous smelting processes (silver, lead, etc.), but especially copper and gold from the foreign ores. The sulphur which is present in the ores in great quantity is applied as much as possible to the manufacture of sulphuric acid, as also the greater part of the arsenic present in the ores is converted into various products of the arts. White arsenic (arsenious acid), red arsenic (realgar of commerce), yellow arsenic (orpiment of commerce), and black metallic arsenic (so called cobaltum or Fly stone). They have also turned their attention recently, with good result, to the experimental production of zinc from the ores rich in that metal. The percentage of silver in the Freiberg ores comes especially from more or less finely divided silver-glance, polybasite, stephanite, ruby silver ores, and silver Fahlerz. Silver occurs also occasionally though seldom, native, as a wiry, hair-like mass called washed silver, and in combination with arsenic, tellurium and antimony. Lead occurs only as Galena in these ores; copper as copper pyrites, peacock ore, and copper; Fahlerz and the other ores only as combinations with sulphur, never oxidized. The constituents of these ores of secondary importance, which constitute the gangue, are iron pyrites, arsenical pyrites, zinc blende, and earthy substances, such as quartz, lime, fluo spar, heavy spar, and brown spar. A great part of the Freiberg ores contain traces of gold, cobalt, and nickel, but not in paying quantity.

METALLURGICAL DIVISION OF THE ORES.

All the ores are divided into

1. LEAD ORES.—Ores (without exception argentiferous) which make about one-third ($\frac{1}{3}$) of the entire production of the mines. These are divided again according to their percentage of lead, or the amount of their valueless constituents, into

- a) Plumbiferous ores, and
- b) Glances (or galenoids).

While the percentage of lead in the former varies between fifteen and twenty-nine per cent., and the percentage of the valueless constituents, such as iron pyrites, arsenical pyrites, zinc blende, and quartz, exceed it; in the latter it goes from thirty per cent. to the highest percentage of lead possible, and the gangue is only represented in small quantity.

Pure Galena (PbS) contains stoichiometrically 86.61 per cent. lead; but it never occurs in nature with so high a percentage of lead. The average percentage amounts to about 40 per cent. lead and 0.15 per cent. Ag.

2. DÜRR ORES—These are the real silver ores, which contain no lead and copper (at least in paying quantity), and frequently consist entirely of earthy gangue. As these so often contain arsenical pyrites, iron pyrites, and zinc blende, they are divided according as one or the other of these predominates.

- | | | |
|-----------------|---|------------|
| 1st. Silicious, | } | Dürr Ores. |
| 2d. Spathic, | | |
| 3d. Pyritic, | | |
| 4th. Blendic, | | |

The silver in these varies from two-hundredths of a per cent. (0.02 p. c.) several per cent.; so that among them occur the richest ores that are brought to the furnace.

3. COPPER ORES.—These are also always argentiferous, but occur *comparatively rarely*. Their percentage of copper varies between 1 per cent. and 10 per cent.; is in the average, however, about 3 per cent. Their constituents of secondary importance are mainly pyritic and blendic. Copper ores with a high percentage of copper are scarcely

ever produced by the Royal Mining Works; but often very rich ores are obtained from foreign countries—chiefly America.

The above three classes of ores are united under the general head of “paid ores,” because their purchase is regulated by the established price which the smelting works pay for each metal.

The sulphur and arsenic in these ores are paid for when the material is furnished in lumps, and not pulverized. In such ores the sulphur is paid for when it exceeds 20 per cent., and the arsenic when it exceeds 25 per cent. In contradistinction to the “paid ores” are:

4. THE “REAGENT ORES.”—The purchase of such ores takes place only conditionally on the need which may be felt for them in the different smelting processes, and on the basis of any agreement made between the smelting works and the particular mines furnishing them. All those ores belong to this class, whose percentage of silver varies from one to one and a half hundredths of one per cent. (0.01–0, 0.015 p. c.), provided that a percentage of 15 or more per cent. of lead, or 1 or more per cent. of copper, does not place them among the copper or lead ores.

In these ores also the sulphur and arsenic are paid for under the same conditions as in the “paid ores,” except that in arsenious ores the broken form is not desirable. The constituents of these ores are principally iron pyrites, arsenical pyrites, zinc blende, quartz, calcite, etc.; at the same time they always contain small quantities of copper and lead. According to these constituents, these are called pyrito-blendic, silico-pyritic, and silico-blendo-pyritic. To the classes of the reagent ores come those Dürr ores, which contain but little silver (up to 0.04 per cent. when 15 per cent. and upwards is present).

The furnishing of the ores is performed with them either *dry* (1st) dry stamped, (2d) in lumps, as is the case with the reagent ores, or in a moist condition (jigged or washed ore). In the stamped ores, besides a careful mixing, such a size of grain is required, that when it is sifted in a sieve of 675 meshes to the square inch not more than 15 per cent. remains behind.

In wet ores it is required that they be as free as possible from hygroscopic water; that they can be weighed with certainty, and permit the obtaining of a reliable average analysis; and that they be neither in a viscous nor liquid condition.

I. THE LEAD PROCESS IN CUPOLA FURNACES.

The object of this process is, after previous roasting of the argentiferous Dürr ores, Galenoids, and plumbiferous ores with the proper reagents in a roasting furnace, so to smelt them in a cupola furnace that the silver is extracted by the lead (raw lead), and further that there is produced a combination of different sulphides of the metals (lead matt), and when the ores contain nickel and cobalt, also a combination of arsenides of the metals (lead speiss); on the other hand, the earthy constituents and less easily reducible metal oxides combine to form a slag (lead slag).

COMPOSITION OF A CHARGE.

The ores which come to the lead process are:

1. All the lead ores (Galenoids and plumbiferous).
2. All the Dürr ores from 0.1 per cent. Ag. upwards.
3. Copper ores from 0.1 to 0.15 per cent. Ag. upwards, when the percentage of copper does not exceed 6 per cent., because otherwise the raw lead produced would be rendered too impure by the copper, which has a powerful affinity for lead.

The above ores are then sorted and mixed. By sorting is understood a mixing together of those ores which contain, and are treated for the purpose of extracting, one and the same metal, but whose various percentages of this metal are different, and which behave differently in the furnace.

For example, in Freiberg all lead ores are *associated together* and mixed with the Dürr ores, which in their turn are associated together among themselves, as they possess different percentage of silver and different earthy constituents, and also behave differently when smelted. By mixing is understood a mixing of the ores which are to be treated, with the reagents, such as calcite, heavy spar, old slag, or some already existing middle product of the smelting works.

OBJECT OF THE COMPOSITION OF THE ORES.

The objects of the sorting and mixing, or composition of the ores, are :

1st. In order to obtain a quantity of the metal or product (raw lead, raw matt), which experience proves to be most advantageous, and, what often depends upon this, to procure in the product (*i. e.* raw lead) a certain definite percentage of silver.

2d. In order to obtain a good run, in which the earthy constituents of the ore unite in a fusible slag, which would not be the case if each kind of ore was smelted by itself. The weight of one of these mixtures, which are kept ready in the mixing house, is from 2000 to 3000 centners, of which 80 per cent. are lead ores and 20 per cent. Dürr ores (including copper ores, if such are present). The amount of lead in such a mixture varies between 30 and 40 per cent. of lead ; that of silver, 0.15 to 0.18 per cent.

Very rich Dürr ores are excluded from this composition. They are strewed on the floor of the charge room amongst the other ores, as these latter are used up, and from time to time again sorted and mixed, in order to avoid as much as possible mechanical loss. The separate charges are transferred in wheelbarrows from the ore house to the charge house, and dumped in alternate thin layers of lead ore, copper ore, and Dürr ore on the floor. From a heap thus made the mixer takes vertical slices with a shovel, and throws them together in the form of a cone in some other place. To make the mixing still more complete, this operation can be repeated. This mixed mass is pushed from here in iron cars (railroad cars) over the roasting furnace, and dumped there. The dry stamped ores are moistened before this mixing, in order to prevent the raising of too much dust.

II. ROASTING OR PREPARATORY WORK WITH THE ORES AND SOME ALREADY FORMED PRODUCTS.

The object of roasting is an oxidation of the metals which are combined with sulphur and arsenic, and a volatilization of the above inflammable bodies up to a certain point. A complete volatilization of these materials is not intended. The roasting of the lead process charge can be undertaken either,

1st. In double roast furnaces, or in combined hearth and muffle furnaces.

2d. Of late years principally in "forward-shoveling" roast furnaces.

The real roasting space of the double roasting furnaces, or hearth and muffle furnaces, consists of the hearth and the muffle. The hearth is alongside the fire-place, which latter consists of grate and ash box, and the fire-place is separated from the hearth by a bridge made of bricks. The muffle lies over the hearth, and is entirely separated from it, but is heated by the flame which passes both below and above it. The under hearth is ten feet long and five feet six inches broad (Saxon measure). The roof of the hearth consists of three strong slabs of slate, which rest on three arches, which in turn abut against the longer sides of the furnaces. These slabs form at the same time the floor of the upper hearth or muffle, which, with the exception of three working doors, some air holes, and an opening for the roast gases, is closed on all sides, like a real muffle.

The sole of such a muffle is thirteen feet long and six feet broad. The products of combustion of the stone coal, mingled with the gases arising from roasting these ores, escape from the lower hearth, and pass through a chamber above the muffle, which thus acts as a dust-condensation chamber. At the extremity of the furnace it enters a canal, which connects with a subterranean passage leading to a chimney 150 feet high. The gases from the muffle, on the contrary, escape separately through a long canal to a set of terrace-built condensing chambers, which they traverse, uniting with the other gases behind these chambers, when all go together to the 150 feet chimney.

In these long Canals and Dust condensation chambers (which latter are erected above ground, and provided with a roof of iron plates for the better cooling off of the vapors, but in other respects built of brick), the roast Gases find ample opportunity to deposit all condensable ingredients, especially arsenious-acid (As_2O_3), and the mechanically suspended little particles of ore dust, which otherwise would pass through the chimney and reach the open air, injuring the neighboring vegetation. In the Muldner Smelting works there are 6 such Furnaces in a row, which are to be altered, as 18 already have been, into "Forward-Shoveling" Roast furnaces.

MODE OF PROCEDURE IN ROASTING.

(The strength (the weight) of) a roasting charge for the Lead Process, amounts to ten Centners (100 lbs. Saxon).

The charge enters the muffle by two holes in its roof, from the drying hearth above it. The charge is here brought to a dark cherry-red glow, and remains perfectly in powder form without agglutinating. After 4 or 5 hours roasting, it is reached through the middle working door, and drawn by a rake down through a vertical shoot ending in the sole of the muffle and generally closed by a slab.

It is then roasted in direct contact with the flame of stone-coal. Here the temperature of the hearth is raised until it loses its powdery state and forms larger or smaller lumps. Meantime a fresh charge is brought upon the muffle, receives its preliminary roasting and is raked down upon the hearth as before described.

There are three periods distinguishable in the course of the process.

- 1) The period of ignition.
- 2) The period of desulphurization.
- 3) The period of complete roasting.

In the period of ignition which takes place in the muffle, the ore loses its hygroscopic water. The charge is allowed to lie quietly in the muffle without turning or raking it, until the beginning of the desulphurization, which arises from $1\frac{1}{2}$ to 2 hours after the commencement ("Burning-out" of the Ore).

In the period of desulphurization the sulphur and arsenic present in the ore, commence to burn and keep the ore in a state of ignition by their own combustion. During this time it is necessary to turn and rake the ore diligently with the roast rake, "crutch," and shovel, in order to keep always presenting new surfaces of the glowing ore particles to the atmosphere, and thus to accelerate the desulphurization. Quantities of vapor of sulphurous and arsenious acids (so called Roast Gases), are developed. The greater part of the period of desulphurization takes place on the lower hearth. This period lasts $3\frac{1}{2}$ to 4 hours, during which the fire must not be increased too much, lest a premature agglutination of particles of ore take place, which would interfere with a proper roasting.

During the period of desulphurization the ore loses the powder form and becomes more and more flocculent and bulky. The last two hours of the period of roasting, constitute the period of *complete roasting*. The charge ceases to emit gases, and must, therefore, be strongly ignited in order to decompose the sulphides of the metals and the sulphates of the metallic oxides. After the completion of the roasting (*i. e.* 8 to 10 hours), the charge is drawn out of some convenient working aperture, at a red glow into a car which has been pushed under the furnace sole, and a sample is taken for assaying; the remainder is dumped into the receptacle for the particular row of furnaces to which it belongs, cooled off with water and left till it is needed for smelting. The charge which is drawn out, must have been roasted down to 4-5 p. c. of sulphur, whereas its percentage was originally about 25 p. c.

For the determination of the percentage of sulphur, a weighed quantity of the charge is pulverized with three times its bulk of carbonate of soda and saltpetre. This mixture is melted up, dissolved in hot water, and filtered into a beaker glass, to which is added a little chemically pure chlorohydric acid; and is then titrated for sulphuric acid. The daily number of workmen to a furnace is six, two going on every eight hours. One looks out for the muffle and the new charge, the other finishes the roasting of a charge, and attends to the firing.

As the muffleman has less to do, they change about every four hours.

The average consumption of fuel in 24 hours is about 7 bushels of hard slaty coal with a large percentage of ash. A bushel weighs two centners.

MIDDLE PRODUCTS OF THE LEAD PROCESS.

1) *Slag*. The aim is to make this a very fusible silicate of the protoxide of iron, the earthy oxides, and the oxides of zinc and manganese with a little lead (in reality about 5 p. c., containing 0.005 p. c. silver). Of this slag a part is used in compounding the new charge, and the rest in extracting silver and lead in the English furnace.

2) *Lead Matt* is a combination of several sulphides of the metals, principally of lead, but containing also sulphides of iron, copper, zinc and silver. The matt contains on the average 25 to 20 p. c. lead, 10 to 15 p. c. copper and 0.1 to 0.15 p. c. silver. In 24 hours about 10 to 12 centners of matt are formed.

The matt is stamped, and roasted in the hearth and muffle furnace, after which it is again mixed with slags and various materials rich in lime, and brought to the cupola furnace, in order to extract as much as possible of the silver and the lead from it, and to increase as much as possible its percentage of copper. It contains the larger quantity of the copper in the compounded charge. The second time the matt is treated, it is called the "modification" of the matt, and takes place after the conclusion of a run, in the same furnace in which the lead process itself is conducted.

(3 *Raw Lead*.—Which collects in the sump of the furnace, after the above two processes, is a lead in which various impurities, such as arsenic, antimony, and copper, exist in greater or less degree. The greater part of the silver of the charge is collected in this raw lead. It contains from 0.6 to 0.8 p.c. of silver and sometimes with very rich Dürr-ores reaches 1 p.c. of silver. About 16 to 18 centners are produced daily. In order to separate the lead and silver, this raw lead is either directly cupelled, or (which is the case except with the very pure ores) it is refined to get rid of the impurities, then submitted to Pattinson's process to concentrate the silver, and finally cupelled when it reaches about 1.5 to 1.6 p.c. silver.

LEAD SPEISS is produced, though more rarely. It is composed of iron, copper, cobalt, nickel and arsenic. If it forms in any quantity, its place is between the raw lead at the bottom and the lead matt immediately above it, so that the order in which these products lie is (counting from the bottom), 1st, raw lead; 2d, lead speiss; 3d, lead matt; and 4th lead slag. It usually adheres to the matt, however, and is submitted to further treatment with the latter, until a sufficient quantity is obtained to make a disc easily raised from the pot, into which the molten mass is drawn off.

The expenditure of fuel per day is thirty to thirty-two bushels of coke.

The force necessary to keep a furnace in constant operation consists of six men, three by day, and three by night, who have twelve hour shifts. They are divided into smelters, assistants, and slag-runners; of each of whom there is one in each shift. The smelter has the responsibility of taking charge of the furnace and conducting the process. The assistant has to help him as much as possible, and especially feed the charge into the furnace, under direction of the smelter. The slag-runner has to remove the slag to the dump heaps, and keep the part of the floor over which it runs, always in order, and free from obstructions.

MODIFICATION OF THE LEAD MATT.

This is always taken up at the close of a run of the lead process. The matt is stamped and roasted as completely as possible, mixed in the slag from the same process, and with furnace ends from the lead process, and smelted in a cupola furnace. There is no definite relation of parts in the mixture. Generally, to about 40 cwt. of roasted matt 80 cwt. slag are added. It smelts very rapidly, because the mixture is very fusible, and is drawn off six to eight times in a day.

The products are :—1st, Slag; 2d, Matt (modification); and 3d, Raw Lead.

The manipulation in this process is the same as in the lead process.

COPPER MATT.—The matt which falls in the treatment of the modified matt, is called copper matt. The object is to increase the percentage of copper, and the partial extraction, at least, of the silver and lead, of which this matt still contains no small amount. This, and the spur process, are undertaken at the end of a lead matt run, in the same kind of furnace as in the lead matt process. The matt is stamped or roasted, and smelted with litharge reduction slag, and a small percentage of fluor-spar, lime and slag of the same process. Care must be taken with the roasting, as this matt melts more easily than lead matt, on account of its higher percentage of copper. In twenty-four hours, about 60 centners of copper matt, or about 30 centners of spur matt, are produced; but besides these, raw lead and some speiss, which latter goes to the lead matt process.

CONCENTRATION PROCESS.—By means of spuring, the matt has been brought up to 40 to 50 per cent. of copper; and in order to increase the percentage of it still more, it is now concentrated in the reverberatory furnace. Reagents are added to it, calculated to evolve a concentration of copper matt as free as possible from iron, and suitable for vitriolizing. It is stamped and roasted, and mixed with quartz and heavy spar (or barytic slags from previous runs). The use of the baryta is to assist in slagging off the iron; the principal object of the process being to reduce the percentage of this metal to a minimum.

The separation of the silver and lead is really of secondary importance, because these metals are entirely collected in a residue left during the course of the next operation, or that of vitriolization. Charges contain 18 to 20 centners of matt (of which by far the greater part has been washed), and 10 to 12 centners heavy spar and quartz—the latter about one-half to two-thirds of the mass. As before stated, this can be replaced by barytic slags.

SPEISS PROCESS.—The plumbiferous and pyritic material excerned in the course of the lead and spur matt processes, containing 0.4 to 0.5 per cent. of silver, and 1 to 2 per cent. of nickel and cobalt, is made of value by the speiss process. It is mixed with the hearth of cupellation and barytic slag from the concentration-copper process, besides some heavy spar. There result from this, speiss with 12 to 13 per cent. of nickel and cobalt, and copper matt.

This raw speiss is subjected to two or three meltings with various reagents, such as litharge, cupellation hearth, highly silicious slags and heavy spar, and finally becomes a speiss with about 0.03 per cent. of silver, 15 per cent. of copper, and 15 to 18 per cent. of nickel and cobalt. This operation is called the desilverizing of the speiss, or the separation of silver from it. The thus desilverized speiss is placed in a small reverberatory furnace with 50 to 60 per cent. heavy spar, and 20 to 25 per cent. quartz, and refined. The result is a copper matt, and a natural speiss, almost free from iron, with about 40 to 50 per cent. of nickel and cobalt, and 10 per cent. of copper. This product, which is an educt in so far as it is not further treated at the Freiberg Smelting Works, commands a good price at the cobalt blue manufactories.

Recently, the refining and desilvering of the speiss have been accomplished at one time. The speiss is refined with heavy spar and quartz, and after the slag is drawn off, about one or one and a half times the amount by weight of lead poor in silver, is added to the molten mass, and stirred well, the fire being increased. After this, the mass is drawn off into some convenient receptacle; and the products are, raw lead, copper matt, and a speiss much richer in cobalt and nickel, and containing 0.01 to 0.02 per cent. of silver.

REFINING RAW LEAD.—This consists in gradually raising the heat to the melting point, and scraping off the less fusible impurities which float, as scum, on the surface of the metal bath. The lead is kept at a low red heat, and air is freely admitted to its surface.

LEAD SLAG, OR RAW PROCESS.—These two names really designate the same process, and they exist because, at the Muldner Works, the lead slag, besides the ores, is subjected to it, while at the Halsbrückner Works only the Dürr ores and reagent ores having less than 0.1 per cent. of silver, are treated in this way, the lead slag from the Pils furnace being thrown away as worthless. Such ores, of course, are also treated at the Muldner Works.

The object here is to collect the small percentage of silver in an iron matt, which is afterwards roasted at the sulphuric acid works, and provides the latter, to a great extent, with sulphurous acid gas, while the argentiferous iron oxide which is the other product, forms the most valuable base for the composition of the slag in the lead process, and exchanges its associated percentage of silver for the sulphur of the Galena, in the evolution of the raw lead. In the following remarks, the lead slag process will be considered, but it is to be understood that it differs from the raw process only in admitting to the same treatment the product from which it derives its name.

THE PATTINSON PROCESS, OR THE CONCENTRATION OF SILVER IN THE RAW LEAD.

This process was invented in the year 1833 by Mr. Pattinson, of Northumberland, originally with the design of desilverizing leads so poor in silver that they could not be economically cupelled. More recently, this process has also been applied with advantage to leads rich in silver. The plan is to make a lead richer in silver, which diminishes, firstly, the volume of lead to be subjected to cupellation; and secondly, the loss of lead. The plain explanation of the principle underlying this process is as follows:—

A lead containing some silver is melted up in one of a row of large iron kettles, capable of containing from 200 to 250 centners (20,000 pounds, or 10 tons), and then allowed slowly to cool, the fire being withdrawn. While the molten lead is slowly cooling, it is carefully stirred by means of a large perforated iron ladle. In cooling, numbers of crystals are continually being formed and deposited in the bottom, the mother-liquor, or that part which remains molten, containing more silver than that which crystallizes out. The ladle is run down the sides, and scraped over the bottom of the kettle, and then drawn up slowly, and struck once or twice to permit the mother-liquor to run out through the perforations. The crystals are then transferred to the next kettle to the right hand. The consequence is, that at one end of the battery or row of kettles, almost pure lead is obtained, while at the other the required richness, 1.4 to 1.5 p. c. is reached.

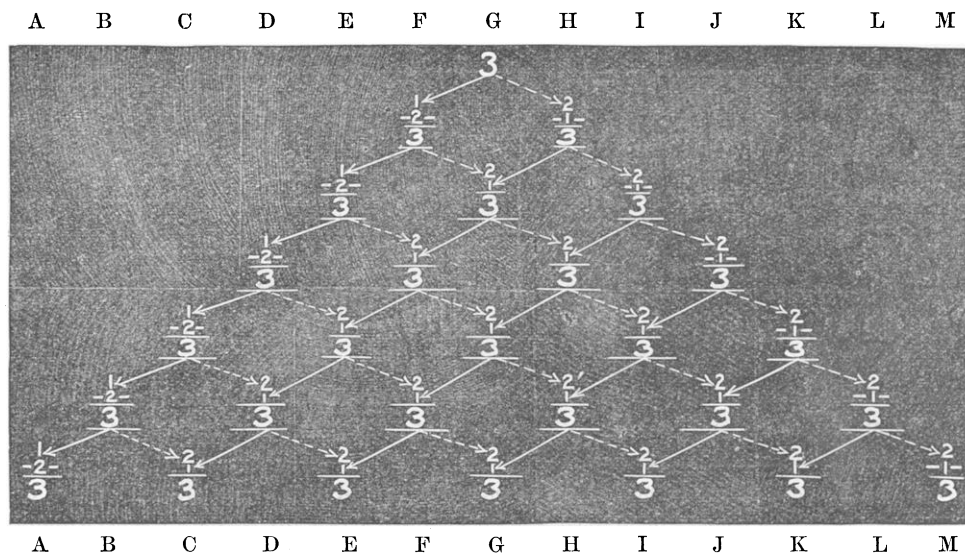
The purity of the lead has especial influence on the working of the process itself, so that the lead which is subjected to Pattinsoning must first be refined, in order to remove the arsenic, antimony and sulphur which it contains. The latter substance especially must be guarded against, as it not only interferes with the proper course of the work, but destroys the kettle itself, as a refining experiment with one of these kettles in Freiberg, and the fate of a whole battery of them, under the charge of an incompetent man in the West, abundantly prove.

The point to which it is possible to carry the separation by this method is about $2\frac{1}{4}$ per cent. of silver, according to experiments conducted at these works. Here the formation of crystals becomes slower and slower, and the still molten mass shows an unmistakable tendency to congeal and harden into a perfectly homogeneous mass. The explanation of this is, that up to this percentage the melting point of the alloy is lower, but above this it is higher than that of lead. Certain it is, that the melting point of an alloy of equal parts silver and lead (or even three parts of lead and one part of silver) is higher than that of pure lead.

The process can be undertaken either with or without intermediate crystals.

1. THE TWO-THIRD SYSTEM WITHOUT INTERMEDIATE CRYSTALS.—The following is the manipulation of the two-third system without intermediate crystals :—

After the lead in the kettle has been melted, and the scum forming on the top (copper, arsenic and lead) has been removed, the fire is almost entirely raked away, and the fire-door under the kettle opened. Water is then carefully sprinkled on the surface of the molten lead bath. This causes the lead near the edge of the kettle to solidify. These solid lumps are broken off and stirred into the rest of the lead, by which means the temperature of the whole mass is evenly lowered. When this lowering of temperature has reached a certain point, the mass becomes viscous from the beginning of the formation of crystals (which are small octahedra). Two workmen now grasp the ladle, and sink it into the kettle, along the sides and bottom, over which it is scraped to collect the crystals deposited there. It is then raised by making a fulcrum of the rim of the kettle. Here it gets two good shakes, to force out the liquid contents of the ladle through the holes. The ladle and its contents are then slid over to the next kettle to the



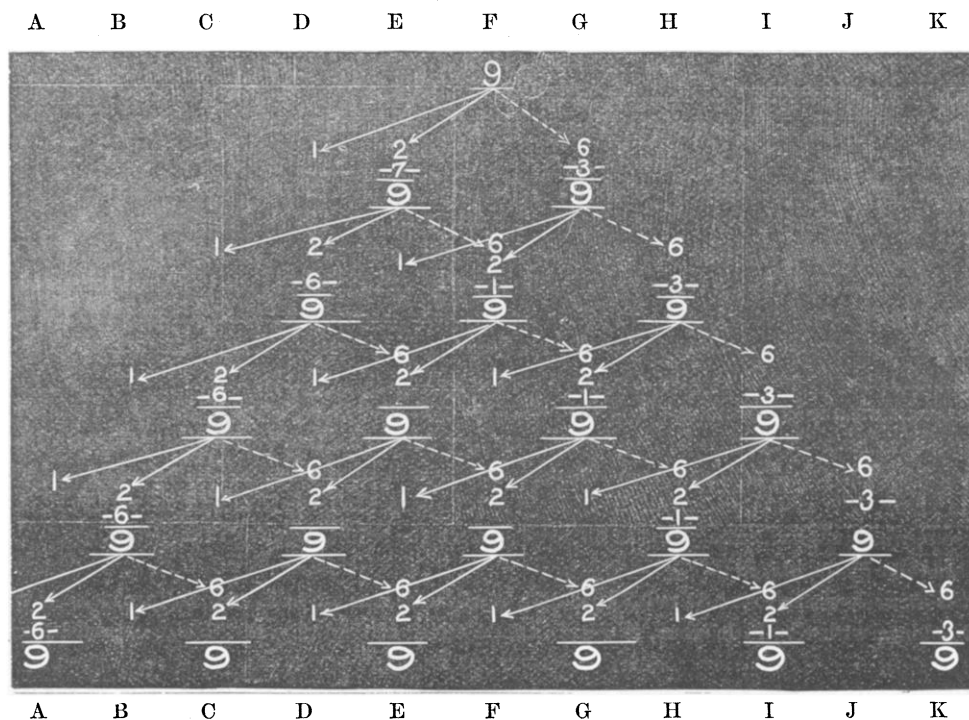
right, on a movable traveller, and the crystals are turned into it. This kettle has been already heated, so that they melt immediately on being placed in it. When two-thirds of the original contents of the kettle have been transferred to the kettle to the right, the remainder is ladled in a liquid state into the kettle to the left. This latter one-third is, compared to the original mass in the first kettle, rich in silver, and the two-thirds which have gone in solid crystals to the right comparatively poor. These two are now treated in the same way, the two-thirds crystals from the kettle on the left being ladled into the middle kettle in which the operation began, into which comes also the one-third mother-liquid from the kettle on the right, while one-third still richer mother-liquid goes into the next kettle to the left, and two-thirds still poorer lead crystals go to the kettle still further to the right. Soon the whole battery is in operation, the alternate kettles, at the close of any one operation, being empty, and the same kettles, at the close of the next step, full. In order to fill up the kettles into which respectively one-third and two-thirds of a charge have been put, refined lead, of various percentages of silver, is stamped, assayed and distributed to the different kettles

of the battery ; so that lead of the required percentage is always on hand to fill up any kettle. In order to comprehend this more clearly, let us suppose the battery to consist of the kettles *A B C D E M*, and let 3 = capacity of each kettle.

Assume that lead of a known percentage of silver is introduced into the middle kettle of the battery (G). Then 2 of crystals go to H and 1 of mother liquor to F. Each of these is filled with lead of a richness corresponding to that of its contents, and the process is continued by allowing F and H to crystallize, whereby 2 from F are transferred to the now empty kettle G, and 1 to E. From H, 2 are carried to I and 1 to G, which is just filled from the two kettles next to it. This is continued, the number of kettles increasing until lead of the required silver-percentage in one end, and of the necessary purity at the other, is obtained. In the above diagram the numbers between two dashes represent thirds of lead which have to be added from lead at hand to fill a kettle, but are not transferred from any other kettle. The $\frac{2}{3}$ of a kettle which are carried as crystals to the right, are indicated by dotted lines ending in arrow heads ; the full lines ending in arrow heads lead to the one-thirds, or the richer mother liquor.

2. TWO-THIRDS SYSTEM WITH INTERMEDIATE CRYSTALS.

By this system $\frac{2}{3}$ of the contents of the first kettle are transferred to the neighboring kettle to the right, as before, in the form of crystals, but after this is done the remaining mother liquor is treated in the same way ; the first two-thirds of the one original third ($\frac{2}{9}$) being transferred as crystals to the first kettle to the left, and the remainder $\frac{1}{9}$ being ladled, as the mother liquor, into the second kettle to the left, as thus :



It will be observed that each of these kettles represents a certain percentage of silver. The next to the last kettle on the "rich lead" side is crystallized, without intermediate crystals. During the process a button is obtained from each kettle, for analysis, in order to ascertain exactly how the concentration is proceeding. At every kettle there are employed two workmen who complete two crystallizations. One fireman attends to firing the furnaces of the battery under direction of the foreman.

"POLING," OR THE PRODUCTION OF TYPE METAL.

The Abstrich obtained by scraping off the scum which forms in the Lead Refining Process after the mere mechanical impurities of the first fifteen minutes of melting have been removed, is divided into two parts. (1) The Abstrich which is formed during the first half of the time. (2) Abstrich. (Abstrich consists, in general terms, of arseniates and antimonates of oxide of lead.)

The desilverization of the 1st abstrich consists in melting it in a refining furnace, whereby the raw lead which has been mechanically mixed with the abstrich is liquated, while the abstrich itself, remaining unmelted, floats on the surface and can be scraped through the open door of the furnace into iron pans.

The lead which is thus separated is drawn off into a hemi-spherical kettle with a long nozzle, and is poured by means of this into a series of radiating lines of iron moulds. The desilverized abstrich is melted in cupola furnace with coke to a lead tolerably rich in antimony. In order to get rid of the copper still more completely and to obtain a product in the form desired for commerce, it is again melted gradually in a Pattinson kettle, and the lead is entirely freed from copper by successive formations of "Schlicker," aided by stirring with a pole of green wood. The heat decomposes the wood, and the gases and steam which rise through the molten metal occasion a still further agitation of the particles and bring every part to the surface. In place of poles an iron cage filled with faggots of green wood, and fastened to the end of a long screw fitting into a nut which is supported by two iron rods to uprights in the masonry around the kettle, is employed. Two arms like those of a letter press allow the cage to be raised and lowered, and at the same time turned round and round in the molten mass.

CUPELLATION.—This operation consists in a further manipulation of the Raw Lead from the Lead, and Lead Matt Processes after its refining and concentration. The plan is to separate the lead and silver by an oxidizing, melting in contact with flame, on a covered hearth and with the aid of an artificial draught. The air admitted through the tuyeres oxidizes the lead, and the melted oxide being specifically lighter than pure lead floats on top and is easily separated from it. In this way the silver, which is with difficulty oxidized, is obtained comparatively free from impurities, and containing from 90 to 95 p.c. of silver.

The construction of a cupellation furnace being generally understood needs no mention here.

After the melting of the lead the fire in the furnace is increased.

The fuel consists of split faggots. About 5 to 5½ cords are consumed in cupelling 350–380 cwt. of lead in 75 to 80 hours, counted from the time the lead was put in the furnace. At the same time the fire is increased, the blast is increased also. Supposing the lead not to have been entirely refined, an abstrich is first formed on the surface of the molten lead, and is drawn out with the scraper (a small round piece of wood, 6 inches in length and 1 to 2 inches in diameter, fastened crosswise to the end of a long iron bar).

After these impurities have been removed, the real litharge formation begins, and the molten oxide is run off by means of little cuts made in the dam of clay by the working door. An iron mould in the shape of a rectangular prism lacking 3 sides is placed with one open side against the wall of the furnace immediately under the working door, and in filling, this mould cools, and the litharge is transported in large blocks of from 16 to 17 centners to an adjoining room, which are broken in pieces in order to separate the red litharge from the yellow.

These are to be distinguished:—

1. *Yellow litharge*, with about 0.04 to 0.05 per cent. of silver, is smelted in the cupola furnace.
2. *Red litharge*, with very little silver, is found in the interior of the lumps of litharge obtained from the cupellation.
3. *Separation litharge*, which is produced just before the silver blicks; *i. e.* the last portion of the lead separates from the silver, and the latter suddenly assumes a bright, clear surface.

As the surface of the molten lead becomes continually lower, it is necessary to cut the groove for the melted litharge deeper and deeper, and great skill and experience are required to prevent the rich lead escaping with the litharge. The absorption of the liquid lead into the sole of the hearth gives rise to the formation of bubbles of carbonic acid from the calcareous mass of which it is composed, and this gives the cupeller a means to guide him in running off the litharge. The groove is not cut till this border of bubbles is about two inches wide. After so much litharge

has run out of the first groove that the litharge mould has been filled three times, the groove is closed, and enough refined lead is added to bring the contents of the furnace once more to the old level. Another groove is then cut near the first one, and three moulds are filled through this; after which a third groove is cut still further to the left, etc. After this, when the requisite amount of lead has been added, the first groove is again opened, &c., till each groove has been used three times, at each time filling three moulds of 16 to 17 centners each, which makes $16 \times 17 = 432$ centners.

The amount of air conducted through both tuyeres per minute is equal to 180 cubic feet.

The charge of the cupellation furnace during the litharge period requires very great skill and experience from the cupellers. As the surface of the lead sinks more and more, the tuyeres must be more and more inclined to bring the current of air upon it. There seems to be no difference between the chemical constitution of red and yellow litharge. According to the most accurate results yet reached, the proportion of red lead which is obtained appear to depend upon the purity of the lead and the length of time it takes in cooling.

The nearer the process approaches to the "Blick," the slower is the formation of litharge, till at last it can only be continued by a very strong fire. With the exception of this part of the litharge period, the temperature during that period must be lower than during the formation of "Abstrich," with which cupellation begins.

SILVER BLICK.—When the molten litharge becomes so small in quantity that it can no longer cover the surface of the silver beneath it, the mass becomes suddenly very bright, and shows the sea-green color of melted silver.

Figures like flowers and waves appear on the surface of the molten silver, and are occasioned by the covering of fused litharge forming no longer a continuous sheet on the bath, but becoming more and more net-like, while the bright silver below shines more and more through the openings, till finally the last particles of litharge are driven to the edge of the hearth. This is the juncture to which the name "Silver Blick" has been applied. As soon as this appearance ensues, the fire is quenched quickly by throwing pails of water upon it, the blast is stopped and hot water is poured upon the "Blick Silver" by means of an iron trough in order to cool it as rapidly as possible.

When the "Blick Silver" to be obtained, is too heavy to be easily handled, a "silver knife" or thin iron beam with several branching arms on each side, is lowered down into the metal before it hardens, so that it can be easily broken in pieces. Without this arrangement it would be very difficult to break the silver, and considerable loss would be likely to ensue in the effort to do so. The cover of the cupellation furnace is lifted off and swung to one side, and the silver is removed to some place of security until ready for refining. This "Blick Silver" contains still 4 to 5 p.c. of impurities, chiefly copper, lead, and bismuth, the latter having even a greater affinity for silver than lead. The weight of one of these "Silver Blinks" is from 2 to 6 centners. Only a small part of the silver goes into the hearth or elsewhere into the plumbiferous products of cupellation.

The sole of the hearth which is soaked with oxide of lead to a depth of 2 to 3 inches, breaks off in separate scales from that portion of the mass into which the litharge has not penetrated. It is known simply as "Hearth," and is either treated in the Lead Matt Process as a reagent, or is smelted in cupalo furnaces by itself with coke to a pure Raw Lead, the earthy constituents of the hearth mass forming a slag very difficult to fuse. The part of the hearth which has not been in contact with the molten litharge is broken up and used together with new material in the formation of the next hearth in the cupellation furnace. By the treatment of foreign (American) ores, a "Blick Silver" is obtained containing 0.11 to 0.15 p.c. of gold. This is treated by itself. From the cupellation of 350-380 centners of pattinsoned Raw Lead there result 330 centners yellow and red litharge, of which the $\frac{1}{2}$ to $\frac{1}{3}$ part is red, and contains about 1.5 p.c. Silver. Red litharge is packed in kegs and sold, while the yellow is reduced to pure lead. The weight of the cupellation hearth is from 38 to 40 centners.

The "Blick Silver" before reaching the fineness required for the mint must be still further refined.

Refining of Blick Silver.—This work consists of a continuation of the cupelling process, whereby the Silver is so far purified from the other metals that it can be immediately used by the mint without further refining.

The silver refining furnace in which this operation is conducted very nearly resembles the English reverberatory furnace, but is smaller. It has, besides, a blast through two tuyeres situated near the fire bridge and one on each side

of it, and instead of the immovable brick vault over the hearth a movable iron cover, which, by means of an attachment to a windlass, can be hoisted and moved to one side, as is the case with the cupellation furnace.

It is necessary to prepare the material for its hearth sole at least two days before. It must be sifted as fine as possible and moistened with water. This mass is spread upon the hard burnt fire brick, and after being pounded hard is scraped into a basin form, the lowest point being in the middle, and the sole being here $1\frac{1}{2}$ to 2 inches in thickness. In the centre of this basin a hemispherical pot is made in order to allow the silver to collect, and to render the ladling out more easy.

After all these preliminaries have been attended to, a small fire of coke is built upon the hearth in order to dry it, whereupon the cover is put on and luted with clay. Before the Blick Silver can be placed in the furnace, the latter must be not only entirely dry, but shortly before this must have been brought to the highest possible melting heat, as otherwise numerous cracks would appear in the hearth, and the silver would be more difficult to melt.

The hearth must, therefore, be brought to a bright red heat just before the Blick Silver is put in.

For this purpose, 8 or 9 hours before the introduction into the furnace of the Blick Silver, a light fire of stone coal is kindled in the blast furnace, and this is gradually increased until just before the Blick Silver is put in, the furnace has reached the highest possible temperature. In placing the blocks of Blick Silver into the furnace, care is taken to bring them near the fire bridge, where they get the greatest amount of heat. If all has not been put in at once, the remainder is added after the silver already in the furnace has been melted. The working door is then closed by an iron slab, and it, as well as all other apertures luted with clay, and the fire increased.

If after two or three hours the silver is melted, the heat must still be continued, and a weak stream of air must be admitted to the silver bath from the tuyeres on both sides of the fire bridge. From time to time the molten metal is stirred up with the stirring iron, in order to bring all impurities which may be contained in the silver to the surface. Finely pulverized hearth-mass is strewn over the surface, and aids in absorbing the liquefied oxides of bismuth and lead. It is scraped from time to time out of the working door. After several hours, during which the temperature has been maintained uniformly, and the molten metal well stirred, a small quantity is taken out in the assay spoon to ascertain how far the silver is refined. Only when the fracture shows satin lustre and perfectly white color is the silver of the requisite fineness. Next to these appearances is that of the reflecting power of the molten bath to be observed. When any of the implements are held over the surface of the silver, a perfect image must be observed in the latter. Very often it is found that, though the reflection is perfect, the fracture is gray and granular, a proof that the silver has absorbed too much oxygen from the blast. As the silver in this condition is brittle, and not suitable for the purpose of coining, the absorbed oxygen must be got rid of by strewing small lumps of coke of the size of a walnut upon the surface, whereby the oxygen is driven off in carbonic acid. As soon as it is evident that the silver is fine, and can be drawn out without exhibiting cracks at the edges, it is subjected to another high melting heat, in order to bring it into the proper condition to ladle out. Before ladling out, the blast is stopped, and a granular test is taken—*i. e.*, a little of the molten silver is taken out in the assay spoon and poured over the moistened ends of a brich broom into water, when it granulates. This is assayed to ascertain the degree of fineness. This silver is given to the Director of the Works for assaying. After this the silver is poured into iron pans holding 25 to 30 lbs., which must previously be coated with a layer of clay, as must also the ladle itself. The latter is heated red hot before being dipped into the silver, to prevent particles of the precious metal from adhering to it.

In this manner 20–25 centners of blick-silver can be refined in ten to twelve hours, with an expenditure of eight to nine bushels of slaty coal.

If it is desirable to refine more silver, it can be introduced into the same furnaces without changing the hearth. After ladling out, the oxygenated condition of the silver shows itself in the phenomenon of spurting. Silver possesses the curious power of absorbing oxygen in its molten state, and then suddenly giving it up just a moment before it congeals. This gives rise to a spurting of the silver, and to prove that during this phenomenon oxygen is really set free from the silver, it is only necessary to strew coal-dust on the surface of the metal. At the moment of the spurt this coal takes fire, and burns up with great rapidity. The blocks of silver are then turned out of the moulds, and

the little irregularities of surface are smoothed down with a file and brush. Its fineness must be now at least 99 per cent. of silver. It is usually about 99.4, and contains only traces of copper, bismuth, and lead. The degree of fineness is determined by a volumetric analysis.

After the silver has been refined, the little buttons of silver are collected from the hearth, and put aside to be added at the next refining. The part of the hearth into which the oxides of lead and bismuth have soaked (and which contains from 15 to 20 per cent. of bismuth, and 0.15 to 0.2 per cent. of silver) is removed, and submitted to the bismuth separation process.

If the blick-silver is to be treated for gold, it is freed from lead and bismuth in the manner indicated, but, instead of being poured out into pans, it is granulated. The metal is ladled out into a cylindrical copper vessel filled with water. The ladle being filled is moved around and round, and the metal poured out in thin streams into the water, whereby the silver is very finely granulated.

It makes small porous masses of silver, and in this form is most easily attacked by acid. The copper vessel has two pipes, one above and one below. The cold water pours in through the lower, and escapes from this upper pipe. Unless the water is sufficiently cold, granulation will not take place. The separation of the gold from the silver is undertaken exclusively at the Halsbrückner Smelting Works, and consists in the treatment of the granulated and refined blick-silver with concentrated sulphuric acid and the addition of heat, whereby the whole of the silver is dissolved as "silver vitriol," while the gold which was combined with it remains behind in the form of a powder. The operation is performed in a dissolving or separation kettle of cast iron, which is walled in above a blast furnace. The kettle is covered by a copper cap during the application of heat and the period of dissolving, and a pipe is connected with this cover, through which the sulphuric acid vapors are conducted to a small condensation chamber of sheet lead, intended to catch all the little particles of sulphate of silver which may be carried off mechanically. From here the gases are conducted into a chimney. In the copper cover is an aperture through which the contents of the kettle can be constantly stirred. Six centners of auriferous silver are dissolved at one time in such a kettle; and to do this requires 12 centners of oil of vitriol, of which 5 centners are poured in at first, and the other 7 centners added from time to time. In order that the silver may not stick fast to the bottom of the kettle, the mass must be stirred continuously with an iron rod. At first there is a violent disengagement of sulphurous acid, and great care is necessary in firing to prevent the acid from boiling over. In eleven hours the dissolving is finished, and the solution is allowed to stand for ten hours more, in order that it may cool and the gold residue may settle. At the expiration of this time the concentrated solution of sulphate of silver is ladled into copper pans by means of a copper ladle, and transported to a large wooden vessel lined with sheet lead (silver precipitation vessel). It is here stirred with wooden poles; a piece of old copper sheeting is put into the tank, and it is heated by the introduction of steam to a temperature of about 70° C (158° Fahrenheit). The silver precipitates in the form of a grayish-white crystalline mud. In proportion as the metallic silver precipitates, copper vitriol is formed.

Towards the last, the liquor is tested for silver by chloride of sodium. When the dissolving is complete, the liquor is allowed to stand for ten hours, in order to permit the fine particles of silver to settle perfectly, and is then drawn by means of leaden syphons, into a basin where the settling is completed. After this, the fully desilverized liquor is conducted into the evaporation pans, where it is treated for copper vitriol. The "cement silver" which remains in the silver precipitation vessel is sifted in a copper sieve, to get out any particles of copper that may be mixed with it, and is then placed in a tank provided with a false bottom, in which a sufficient number of holes have been made for the escape of the liquid, and is well washed with hot water, until the latter ceases to give with chloride of barium the reaction for sulphuric acid. The waste water is collected, and as it contains sulphate of copper in solution, it is used to dilute future charges of sulphate of silver in the precipitation tank. The thoroughly washed cement silver is then pressed into bricks to expel the water as much as possible, and is brought, in the form of small cylinders, into an iron retort, and heated to redness, to drive off the last trace of water. It is then melted in Graphite crucibles in a blast furnace, with stone-coal in masses of 410—420 pounds, and poured into small cast-iron moulds, which have been smeared with tallow, a test of it having been previously taken to ascertain the degree of fineness. This silver is delivered to the mint with a fineness of 99.9 per cent.

GOLD SEPARATION PROCESS.

If the silver is very poor in gold, two or three dissolvings of six centners refined black-silver each, are conducted in the same kettle, so that the gold of eighteen centners or so is concentrated in it. The gold residue so left is very full of impurities—silver vitriol, metallic silver and anhydrous salts of copper and iron—and for its further purification, is boiled for three hours with concentrated acid, and allowed to cool and settle, the clear liquor being transferred to the silver precipitation vessel. It still contains anhydrous sulphate of copper and iron and metallic silver. It is boiled with hot water in a wooden tank lined with sheet-lead, in order to dissolve the salts. This boiling is repeated three or four times. The wash water of the boiling is precipitated with copper by itself, because a great deal of sulphate of silver is dissolved in it. It is colored green from the iron vitriol. The thus desilverized liquid is used to sprinkle roasted ore. The rest of the wash water of this gold is used like the wash water from the precipitated silver, to dilute the concentrated solution of sulphate of silver. The gold residue is now twice again well digested with 200 pounds of concentrated sulphuric acid in an iron kettle, the first time for eight hours, and the second time for one hour. This is done for the perfect separation of the undissolved silver. From forty centners of this material, enough auriferous residue is obtained to fill two small kettles. This is then put into a porcelain crucible, and boiled with hot water, in order to get rid of the sulphate of silver. The wash water is continually tested for silver.

The gold residue now, for the first time, assumes the brownish-yellow color of finely divided gold. It is well dried on plates of graphite, and then twice heated to redness, after being mixed with sulphate of soda, and boiled with fresh acid. After each boiling, it is boiled with water. It is now melted in a Hessian crucible with saltpetre, to get out any lead that may still remain in it. After cooling, the crucible is broken, and the gold is melted over again in a graphite crucible, in order to free it from the saltpetre slag. It is then poured out, 99.4 per cent. fine, into small cast-iron moulds, in which form it is sold. A pound of gold is worth 466 reichsthaler.

BISMUTH SEPARATION PROCESS.

It has been stated that bismuth exhibits a stronger affinity for silver than does the lead, and it is to this cause that we are to ascribe the marked predominance of bismuth over other metals in the hearth of the refining furnace. This hearth saturated with the last impurities which leave the silver as fused oxides, contains 20 p.c. of silver. It is treated for bismuth as follows: The hearth is stamped fine and digested in the cold, in earthen ware vessels, with equal parts of hydrochloric acid and water, in which the bismuth dissolves, while lead and silver remain in the residue. The bismuth solution is drawn off by means of leaden syphons, and the residue is washed several times thoroughly, the wash-water being poured with the first solution into a large reservoir in which there is sufficient water. The whole of the bismuth is precipitated, as basic terchloride of bismuth, in the form of a white mud. This is then filtered off and dried, after which it is melted in an iron crucible with the addition of calcined soda, coke-dust, and glass-powder, and reduced to metallic bismuth.

VITRIOLIZATION. This process consists in boiling the completely oxidized concentration matt with dilute sulphuric acid, by which treatment the copper is dissolved, and the silver and sulphates of the other metals remain as residue. This solution is allowed to stand and clarify itself, and then crystals are obtained by its concentration. These crystals (so called raw crystals) are dissolved and the solution concentrated again, giving crystals of sulphate of copper so pure as to be fit to bring into commerce.

The concentration matt is first stamped and sifted in order to get the grains as nearly as possible of one size. It is then roasted in the Hearth and Muffle Furnaces, but the muffles are not used in roasting it. The matt is put into the furnace by means of iron boxes. The weight of a charge is 10–12 centners and the length of time of roasting 16 hours. The roasting is begun with a light fire until the matt, by reason of its percentage of sulphur, ignites. During the last 4 to 8 hours it requires a strong fire for the purpose of decomposing the metallic oxides. The charge is turned every two hours (from the chimney to the fire bridge). Besides this it must be well worked over with the shovel and the lumps which are formed, broken up. In front of every working door is a workman who has an eight hour shift. In 24 hours the consumption of fuel is 7 bushels of coal. The concentration matt melts so easily that in spite of the

greatest care portions of it will adhere to the hearth sole, and these portions must be removed by an iron instrument adapted to the purpose. Those agglutinated parts are stamped and again roasted for the oxidation of the enclosed pieces of matt. The roasting is continued for 16 hours in charges of from 10–11 centners. The completely roasted matt is drawn out of the furnace in iron boxes, and transported to a mill where it is first sifted, the fine dust fed through two sets of mill stones by which it is very finely pulverized, is again sifted and then placed in the dissolving tanks. That portion of it which is too coarse to pass the sieves is stamped and roasted again in charges of 10 centners. The solution is conducted in cylindrical vessels lined with sheet lead, and whose bottoms are made of antimonial lead.

There are at present at the Halsbrücke smelting works two dissolving tanks, one great and one small one, the former capable of holding 4 centners of finely pulverized roasted concentrated matt. About 9 centners of acid of the lead chamber (48° to 50° Beaumé) are introduced into the larger of these vessels, and this is then diluted with twice the bulk of mother liquor from previous operations.

The mixture of acid and mother liquor is heated to the boiling point by the introduction of steam, and the roasted and pulverized matt is then stirred in with wooden stirring-instruments in small quantities, while steam is steadily admitted. In three-quarters of an hour the material is completely dissolved. The steam is now shut off, and the liquid allowed to stand a quarter of an hour, in order that the finely divided argentiferous residue may settle, and the saturated solution of 40° – 42° Beaumé clarify itself. In twenty-four hours, eight solutions are made in the larger tank. After the liquid has cleared in the larger vessels, it is drawn off, by means of leaden syphons, into the crystallization tank. Such a tank has a capacity of 100 cubic feet, and holds the liquor of four solutions. All these tanks and vessels are lined with sheet lead.

The argentiferous residue left in the dissolving tanks is well washed, in order to separate the copper vitriol, then washed down through the cock, in the lower part of the tank, and just above the bottom, into a receptacle beneath, where it is again well washed, and then filtered through linen cloth, and finally dried in a furnace, and conveyed to the Lead Process, to extract the silver.

This residue consists in the main of sulphate of lead and metallic silver, particles of sulphur, and anhydrous salts of copper and iron. It averages 30 per cent. of lead, 2 to 2.5 per cent. of silver, and 7 to 8 per cent. of copper. In the crystallization tanks there are suspended numerous bands of lead, to which the crystals of sulphate of copper attach themselves. Crystallization requires from eight to ten days.

These first crystals (raw vitriol), which, on account of the concentration of the solution, are somewhat unsightly in their appearance, are re-dissolved either in water or in mother-liquor, in other lead-lined tanks, heated, as before, by steam.

This liquor is crystallized in the same way, and produces the crystals of copper-vitriol which are required by commerce.

A portion of the mother-liquor which has only a strength of 25° Beaumé more or less, is used to dilute the strong sulphuric acid at the commencement of vitriolization, while another portion is concentrated, by evaporation in leaden pans, to the previous strength of 40 – 42° B., and given over to crystallization. The vitriol crystals from this part of the liquor are dissolved and crystallized again. The mother-liquor of this crystallization contains much iron, besides all the constituents of the matt, of secondary importance, manganese, zinc, arsenic, and a considerable amount of nickel; and it is used to quench the red-hot ore from the roast furnaces. The mother-liquor of the copper vitriol is used again and again to dilute the strong acid, as has been said before, until it becomes so rich in iron that it can no longer be used without rendering the copper crystals impure from that metal.

The pure crystals of copper vitriol are washed in water, to free them from adhering acid, then dried on long shelves, in a room into which warm air is admitted, and finally packed in barrels and sold.

THE MANUFACTURE OF SULPHURIC ACID.

I. *Form and Composition of the Ores and Products rich in Sulphur which are adapted to this Process:—*

There are applied to the production of sulphuric acid,

- 1) The raw matt from the lead slag process : and
- 2) The blende and pyritic Dürr and flux ores which come to the lead slag process. These either in natural lumps (or in agglutinated masses resembling lump ore), or stamped, or pulverized.

The sulphur of the raw matt amounts to 22-25 per cent. ; that of the lump ore, 32-35 per cent. ; and that of the powdered ores, 28-30 per cent. Ore lumps are prepared artificially as follows :—

Rich and infusible ore dust is well mixed in a large wooden tank, and moistened with dilute sulphuric acid. The mass is then worked over with a wooden rake, pressed into iron moulds, cut into small cubes, and dried on the iron slabs over the condensation canal of the roasting furnace. In this manner these acquire such firmness that they can be roasted in kilns just like natural lump ore. The cause of this solidity is to be found in the formation of sulphates of zinc and alumina, compounds which are not easily decomposed by heat.

All these lumps (natural and artificial) are roasted in kilns, but the ore dust is desulphurized in Gerstenhöfer's dust roasting furnace.

The kilns are a kind of cupola furnace in their main features. The inside is a space either like a parallelepipedon, or like the frustrum of a pyramid in form. They are of many different sizes. The high kilns are principally used in the roasting of the raw matt, and the low kilns in roasting the *lump ores* and *ore lumps*.

On the workman's side of these kilns are openings at different heights from the ground, through which the workman can reach all parts of the mass within, by means of suitable iron instruments, and loosen it. The kiln is put in operation by the workman filling it two-thirds full of already ignited raw matt, then kindling a fire underneath, and after the walls of the furnace are red hot, letting in the charge of raw matt through the roof.

The raw matt burns of itself by virtue of its percentage of sulphur. After the lapse of a few hours, a portion of the charge is drawn out of the opening nearest to the sole of the kiln, and this causes the whole superincumbent mass to sink, leaving place at the top for a new charge of raw matt. The new charge is distributed evenly over the surface of the already ignited portion.

About 18-20 centners of raw matt is introduced at once or a charge, and this is repeated about every twelve hours. The introduction of the charge always follows the drawing out of a part from below. The interior of a Gerstenhöfer furnace is a space in the form of a rectangular prism, across which from side wall to side wall a great number of triangular prisms of burnt clay are inserted, with one of their faces upwards.

There are two narrow slits in the roof of the furnace, through which the ore dust is fed through rollers.

Under these slits are two larger triangular prisms, having their edges up, so that the pulverized ore, falling upon these first, is diverted to the right and left, and falls through the entire height of the furnace, resting a short time on each bar. These roast bars must be previously heated to redness by a fire kindled in the furnace itself, but gradually withdrawn as the ore itself ignites.

The powdered ore which collects on the flat sides of the roast bars is ignited by them, and once fairly ignited, evolves such a heat that all other fire is unnecessary. The atmospheric air requisite for combustion is partially introduced through numerous air holes in the workman's side of the furnace, and (in case more air is needed than these can supply) by means of a ventilator. With this exception the furnace is closed, and the products of combustion, of which sulphurous acid forms the greater part, are collected.

The feed is continuous, and 40 cwt. pulverized ore can be roasted in such a furnace in one day.

The gases are first conducted through a condensation chamber, in which the greater part of the arsenious acid condenses, and from here through a subterranean canal (which also serves to condense the still remaining arsenious acid and small particles of ore carried forward by the draught) to the lead chamber, where, by the necessary nitric acid and steam, sulphuric acid is formed. The atmospheric air required to convert the sulphur into sulphurous acid flows into the furnace, and from there it goes with the roast gases into the lead chamber. The amount of sulphurous acid in the products of combustion does not exceed 6-7 per cent. by volume, and indeed in the roasting of the raw matt it is not above 4 per cent. The lead chambers are large rooms lined with sheet lead, in which the formation of sulphuric acid takes place. The lining sheets of lead hang from a strong scaffolding and are soldered together with lead. A "system" of chambers consists generally of one entrance chamber, two main chambers, and two roof chambers which are connected with each other by strong leaden pipes. The entrance chamber receives the nitric acid

necessary for the oxidation of the sulphurous acid. The main part of the process takes place in the two middle intermediate chambers, and the roof chambers are designed to condense the particles which have been mechanically carried by the gases through the other chambers. The roast gases escape here through a chimney into the open air, the greater part of the sulphurous acid having been converted into sulphuric acid. The gases that thus escape are principally brown vapors of hyponitric and nitrous acids, nitrogen and a small quantity of sulphurous acid, and some steam. The steam necessary for the process is generated in a steam boiler outside of the lead chamber building, and is conducted through a cast-iron pipe either through the side or better through the roof of the lead chamber, and it must have a certain tension on leaving the pipe in order that it may disseminate itself over the whole interior space.

The nitric acid which is required in the production of sulphuric acid is made from Chili saltpetre and sulphuric acid of 60° B. The decomposition of the saltpetre (nitre) takes place in close cast-iron retorts, underneath which is a fire place and both ends of which are closed by movable iron doors. 230 lbs. of sulphuric acid and 250 lbs. of saltpetre are put at one time into a retort of this kind and this is repeated every two days. The nitric acid gas mixed with peroxide of nitrogen is condensed in earthen jars (Woulfe's jars) containing water.

From 1 centner of saltpetre 150 lbs. of nitric acid are obtained, or 60 p. c. nitric acid of 36° B. This nitric acid which condenses in the first jar has a strength of 40°–45° B., in the last jar about 15° B. The jars are connected by earthen necks in the usual manner.

As secondary product of this part of the sulphuric acid manufacture are 230–240 lbs. of sulphate of soda (Glauber Salt). At the Muldner works there are three such systems of lead chambers, the first containing 94,000, the second 134,000, and the third 160,000 cubic feet. The lead chambers of the Halsbrückner Works enclose 159,000 cubic feet. In the lead chambers the sulphuric acid is obtained as hydrated acid of 48° to 50° B., and containing a large percentage of arsenious acid. The acid collects in the bottom of the chamber, and must be drawn off from time to time into a basin provided for its reception. For greater facility in observing the strength of the acid, dropping apparatuses are introduced at different places on the sides of the lead chamber where the newly formed acid, trickling down the inside of the walls, is caught and allowed to drop into a little lead cup, from which it is again conducted into the chamber by a leaden pipe. In this way it is easy to test the strength of the acid and thus to regulate the amount of steam, nitric oxide, &c., which are to be admitted. The height of the acid in the chamber is ascertained by means of glass tubes fastened into the sides like the float water-gauge of a steam boiler. If the acid in the little cups shows a tendency to exceed 50° B. in strength, either less nitric oxide gas must be admitted, or the amount of steam increased. A system of lead chambers enclosing 94,000 cubic feet can produce daily 50–60 centners of sulphuric acid of 66° B., and the consumption of nitric acid amounts to 5–6 centners in 24 hours. A system of 160,000 cubic feet can produce 100 cwt. of sulphuric acid of 66° B., with a consumption of nitric acid of 8–10 cwt.

A normal run in this process is indicated partly by the warmth of the leaden walls (occasioned by the chemical processes going on inside), partly from the regular and rapid dropping from the dropping apparatus into the leaden cup before described, and lastly from the brown color of the gases which escape from the roof chambers. In order to be able to observe the color of these gases more perfectly, two small glass windows are inserted into the opposite sides of the chamber.

If the escaping gases are colorless or bright yellow it is an evidence that there is a lack of nitric oxide.

The purification of the acid of the lead chamber from arsenious acid is accomplished by means of sulphydric acid which precipitates it as tersulphide of arsenic. The sulphydric acid is produced from a raw matt free from zinc, which is obtained by smelting lump-ore free from blende without roasting and with slag in a cupola furnace.

This raw matt is broken into small pieces and treated with dilute sulphuric acid in a gas-flask with the assistance of heat from steam which is conducted around the flask. To aid the warming, these flasks are surrounded by iron jackets. The gas is led through a leaden pipe into a waste vessel partly filled with water, whose use is firstly to wash the sulphydric acid, and secondly to furnish a means of observing the course of the operation.

The residue which remains in the gas-flask and which is very rich in silver is carried to the smelting furnace. The solution of iron vitriol resulting from this production of sulphydric acid is evaporated to saturation, and then transferred to crystallization tanks, and crystallized in the same manner as copper vitriol. The centner of Green

vitriol brings one Thaler 10 neugroschen (one dollar). The sulphydric acid gas pours out into the precipitation tower, a large cylindric structure lined with sheet lead, which it entirely fills. Over this precipitation tower is a reservoir containing the still impure acid of the lead chamber which is allowed to trickle into the tower through openings in the bottom of the reservoir. As the acid enters it becomes saturated with the sulphurated hydrogen and the arsenic is precipitated in the form of a yellow mud. The sulphuric acid along with this arsenic mud runs into vats at the bottom of the tower and is allowed to stand till the latter has almost entirely settled, when the former is pumped up again into the reservoir, and again allowed to trickle down the sides of the tower, till a portion in a beaker glass shows little or no arsenic after being saturated with sulphydric acid and allowed to stand for some time. A pumping apparatus is used to carry the purified sulphuric acid from the vats at the bottom to the reservoir on the top of the tower. It consists of a small steam engine with horizontal cylinder, which moves the piston in an air cylinder, compressing the air through tubing in an air tight vat into which the acid has been previously run.

The tersulphide of arsenic is permitted to settle as perfectly as possible in lead-lined wooden tanks, the acid being decanted off as completely and clearly as possible by leaden syphons and run into the evaporation pans.

The yellow arsenic mud is washed thoroughly with water to get rid of the sulphuric acid. This is done in filtering vats lined with lead and provided with numerous apertures in the bottom by which the waste water can escape. The purified arsenical precipitate is taken out to the drying hearth, where it is freed of its water and transferred to the arsenic works for further treatment.

Evaporation of the purified sulphuric acid. This is undertaken in leaden pans, of which there are four on the same level or in terrace form one above the other. The pans must be very shallow to facilitate the evaporation, and the acid must not be more than 12 to 15 inches deep in any part of the vessel.

The degree of concentration to which the sulphuric acid is brought in this operation is exactly 60° B. A stronger acid would attack the lead at that temperature.

The foremost pan in which is the acid of 60° B. rests directly on the iron plates over the fire place. The acid to be concentrated is transferred from one pan to the other towards the fire, so that the last pan into which it comes is directly over the fire place, while the first one filled is furthest from the fire.

The steam from the evaporation, strongly impregnated with acid, escapes into the open air through a long hood connecting with a chimney which is so arranged as to hang directly over the pans.

Stone coal is used as a fuel for the evaporation. This process is continuous, *i. e.*, as much acid is let into the hindmost pan to be concentrated as of the 60° B. acid is taken out of the pan over the fire place. The further concentration of the 60° B. is undertaken in a platina retort of several cubic feet contents. The 60° B. acid is boiled in this platina retort, and the strong acid vapor conducted through an aperture in the platina cover through a helix which rests in a vessel filled with cold water, and into a receptacle under the end of the helix for the collection of the condensed vapor. This is removed to the evaporation pans, and again concentrated with the rest. The sulphuric acid of 66° B. strength being specifically heavier than the weaker acid, sinks to the bottom of the retort, whence it is removed by means of a platina syphon. This acid is run into glazed earthen ware pitchers and filled from these into carboys.

It is 66° B. perfectly colorless and transparent and oily, has specific gravity 1.84, and is tolerably pure hydrate of sulphuric acid. From decomposition of the little organic materials of which the air is always more or less full, it gets very often a brown color. The carboys are covered with willow withes, and are each packed in a box with straw, the neck just protruding a little above the lid. After being filled they are closed by earthen ware stoppers, and sealed with melted sulphur and sand.

The centner of sulphuric acid of 66° B. is worth 2 thalers (\$1.50), exclusive of the packing and carboy which costs 27 neu grochen (67 cts.). Some 60° B. acid is sold also at 1 thaler 12 n. gr. (\$1.05). The cent. of unpurified sulphuric acid of 60° B. is sold for 1 thaler $2\frac{1}{2}$ n. gr. (81 cts.). This is now extensively used to decompose the phosphates in the superphosphate manufactories.

THE MANUFACTURE OF VARIOUS ARSENICAL ARTICLES OF COMMERCE.

The arsenic works are employed in the production of arsenious acid, metallic arsenic, and various sulphides of arsenic. The arsenical dust from the condensation chambers of the Roasting Furnaces furnishes the most of the

material from which these products are derived, but besides these certain Dürre and lead ores, very rich in sulphide of arsenic, are treated directly for this metal. The process is carried on in furnaces closely resembling the English Reverberating furnace with coke as the fuel. The furnace is connected with a very long condensation canal of brick in which the deposition of arsenious acid takes place.

The arsenical dust is brought upon the hearth through two holes in the roof of the furnace in charges of 10 centners, and is then spread out and submitted to a red heat. One workman has charge of such a furnace for 8 hours.

The arsenious acid contained in the dust is sublimed by the high heat and passes from the furnace into the canal. During the sublimation the workmen must continuously stir up and loosen the charge. In 24 hours 40–50 centners of such dust are treated and the expenditure of fuel is 10 bushels of coke.

The fine particles of ore contained in the dust remain upon the sole of the furnace either as powder or in a melted condition, and as they are very rich in lead and contain some silver, they are taken back to the cupel furnaces and mixed with the other argentiferous leads, form the charge for the lead process, but only when they have accumulated to such an extent as to leave no room on the hearth for a fresh charge,

The roasting of the arsenical ores is conducted in a similar manner to the roasting of the pyritic ores in the Reverberatory furnace.

The dearsenized ore is again roasted. The dust which settles in the condensation canal is a fine white crystalline powder. When several hundred centners of this powder have collected in the canal, the latter is cleaned out, the arsenious acid being packed in barrels made of strong staves and lined with paper. The centners is sold for $2\frac{1}{4}$ thalers (\$1.69). It is applied to the manufacture of pigments, and in the manufacture of glass, in dyeing, and lately in enormous quantities in the preparation of aniline colors. That part of the arsenious acid which settles in the part of the canal nearest to the furnace is usually mixed to a certain extent with fine particles of ore dust, which have been mechanically carried along with it, and this is especially used in the fabrication of "White Glass" so called. This "White Glass" is nothing more or less than melted arsenious acid. It is a homogenous mass translucent and slightly yellow to milk white, with conchoidal fracture and strong vitreous lustre. The manufacture of "White Glass" is accomplished in small iron kettles which are placed over the fire place, their rims just reaching the level of the brick roof of the latter. Movable iron covers shaped like stove pipes and narrowing towards the top are placed over these kettles, and connect at their upper ends with the chimney. These covers are 3 to 4 feet in height and about $1\frac{1}{2}$ feet in diameter at the base. The Process depends upon the property of the arsenious acid to sublime before it melts. The heat sublimes the arsenious acid which melts and settles on the hot walls of these covers. When so much has collected there that the gases can no longer find egress to the chimney, the covers are taken off, and the "White Glass" knocked out of them and packed in kegs or barrels lined with paper. Only a small portion of the arsenious acid escapes into the chimney. The impurities remain behind in the bottom of the kettle.

The least admixture of soot or sulphur causes rough and streaky glass. The sublimation point of arsenious acid is somewhere about 230° C.

MANUFACTURE OF RED GLASS.

The ores containing arsenical and iron pyrites are used in the process. The percentage of arsenic varies from 10 to 12 p. c.

The ore is *distilled* in clay retorts similar to those employed in the manufacture of illuminating gas. The sulphide of arsenic sublimed by the fire of stone coal beneath the retorts, deposits in boxes of sheet iron inserted into the small ends of the retorts, partly as powder and partly in a melted state.

The residue which remains in the retort contains very little arsenic, but consists principally of a magnetic sulphide of iron somewhat like magnetic pyrites. It is broken into small pieces, and delivered to the sulphuric acid works to be used in making sulphuric acid. The arsenic collected in the iron boxes is a heterogeneous and variously colored mass, possessing a stony appearance on fresh surfaces of fracture.

In order to convert the material into "Red Glass" it is first purified by melting it up in cast-iron kettles, and

stirring it thoroughly when in a liquid state by means of iron rods in order to bring the impurities to the surface, whence they can be removed.

The desired shade of color is then obtained by adding either sulphur or metallic arsenic.

By adding sulphur the color is made a darker red, and by arsenic a brighter red. On cooling, this material forms a homogeneous mass of cherry red color. In general terms it may be stated to be a sulphide of arsenic, in which the percentges of the component elements vary according to circumstances.

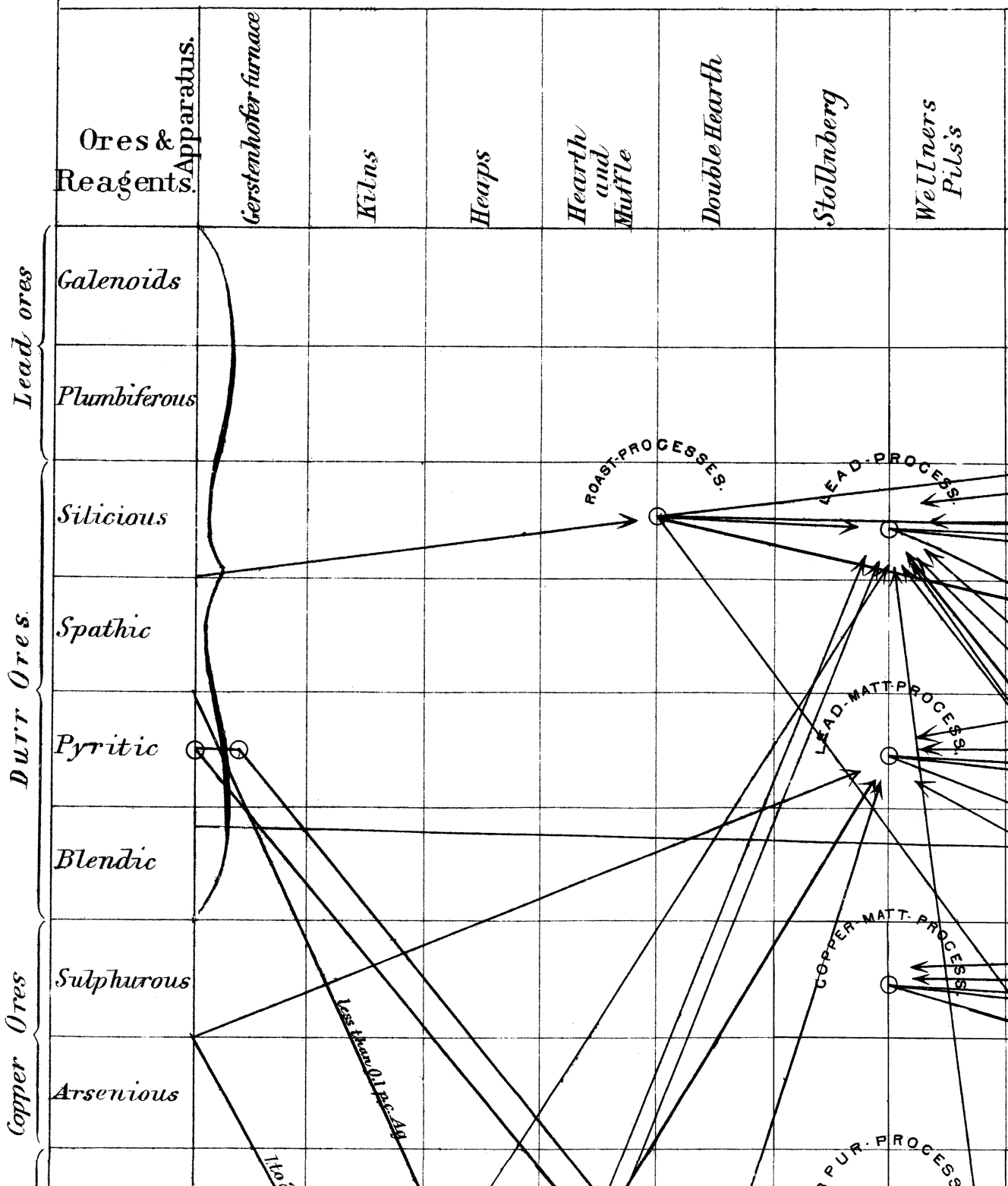
This "Red Glass" is known in the arts as Realgar, and is worth from 12 to 15 Thalers (\$9 to 11.25) per cent.

It is used by tanners to remove the hair from the hides.

"Yellow Glass" is also a sulphide of arsenic with a higher percentage of sulphur, and is prepared in a similar manner.

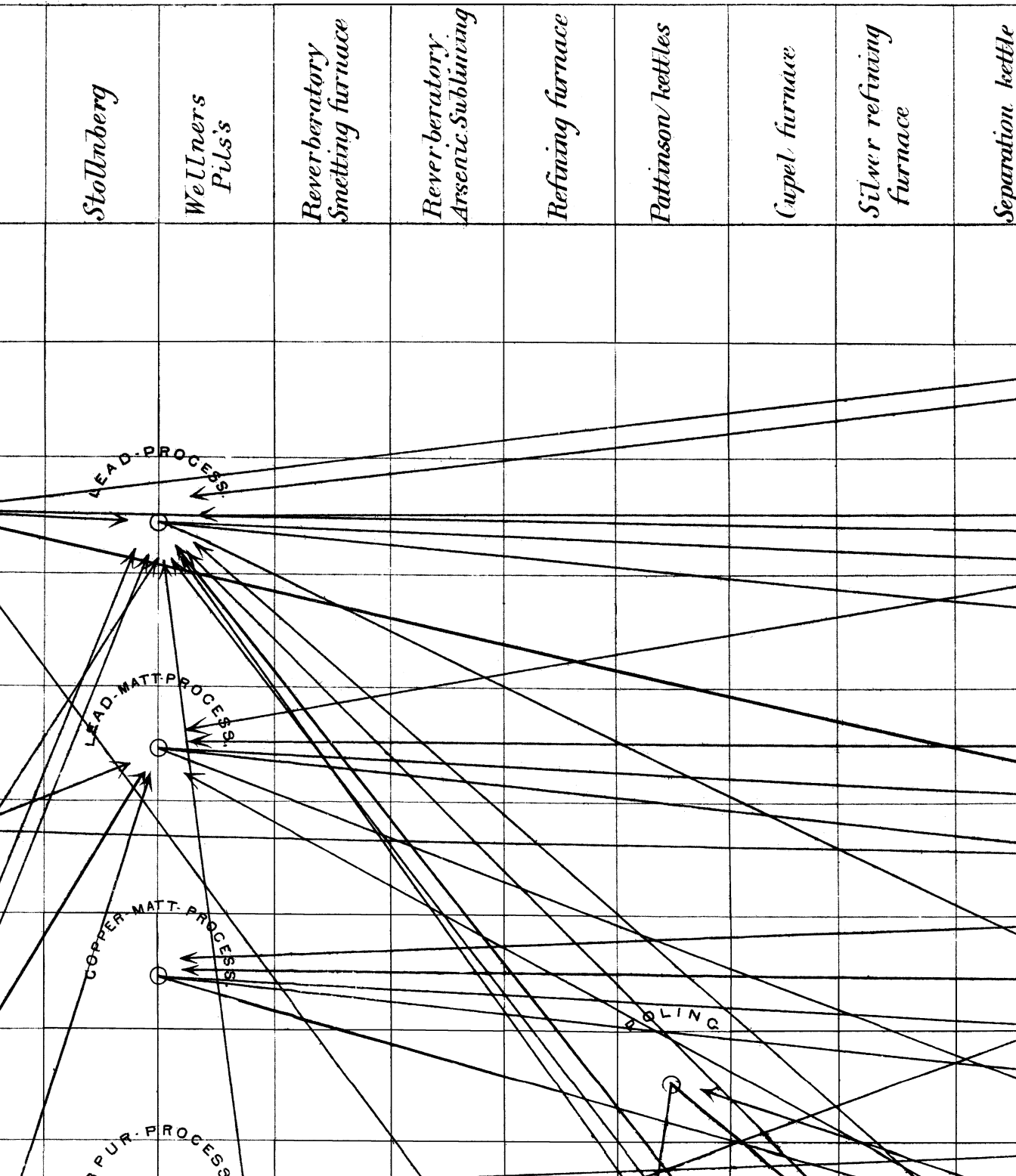
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of the FRIEDBERG SMELT

Designed & executed by Persifor Frazer
read before the American Philosophical Society

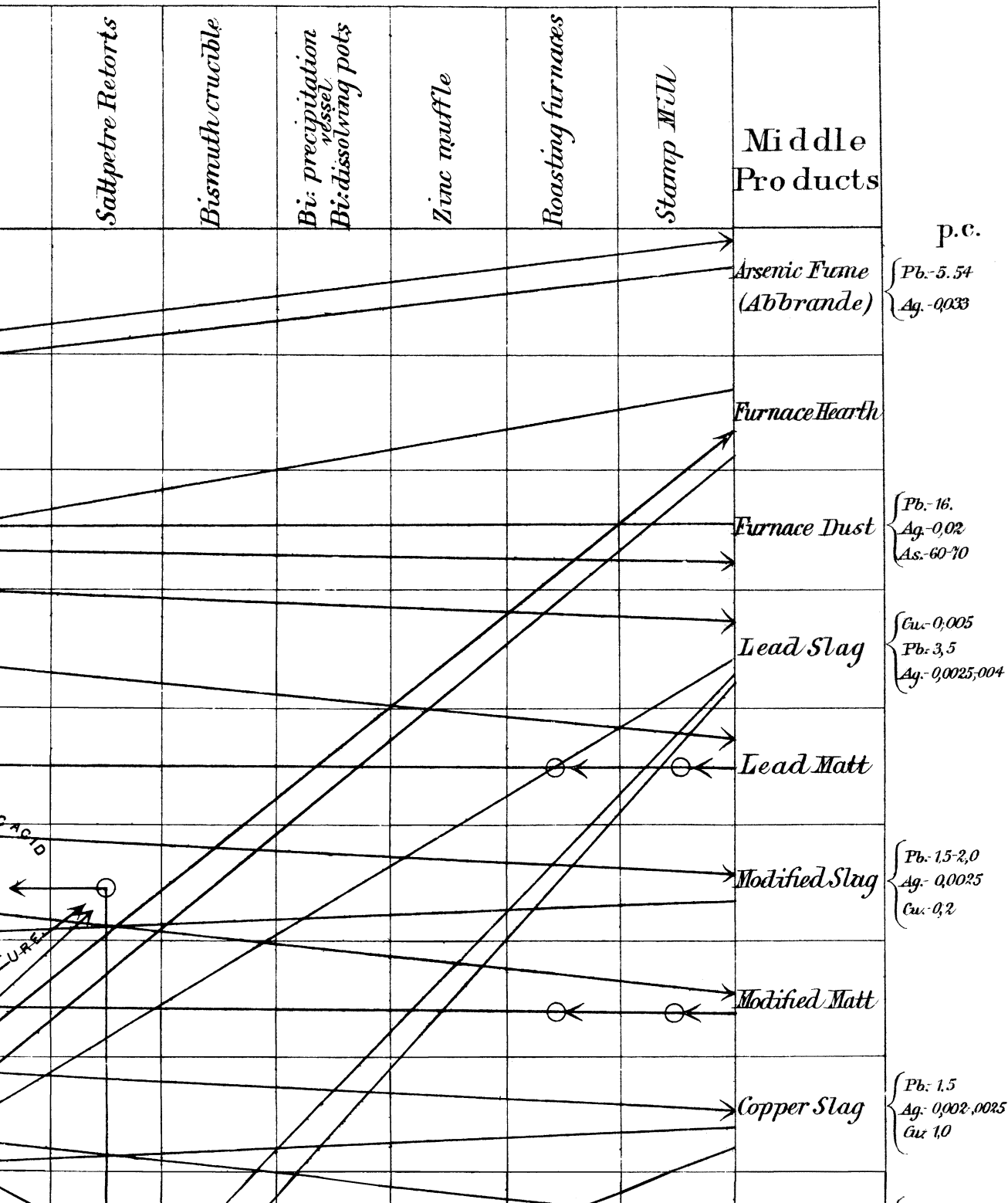


Philosophical Society at Philadelphia, June 17th 1870.

Cupel furnace								
Silver refining furnace								
Separation kettle								
Silver precipitation vessel								
Dissolving tank								
Arsenic Retorts Arsenic crucible								
Lead Chamber								
Saltpetre Retorts								
Bismuth crucible								

PROCESSES.

1870.



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Flux Ores

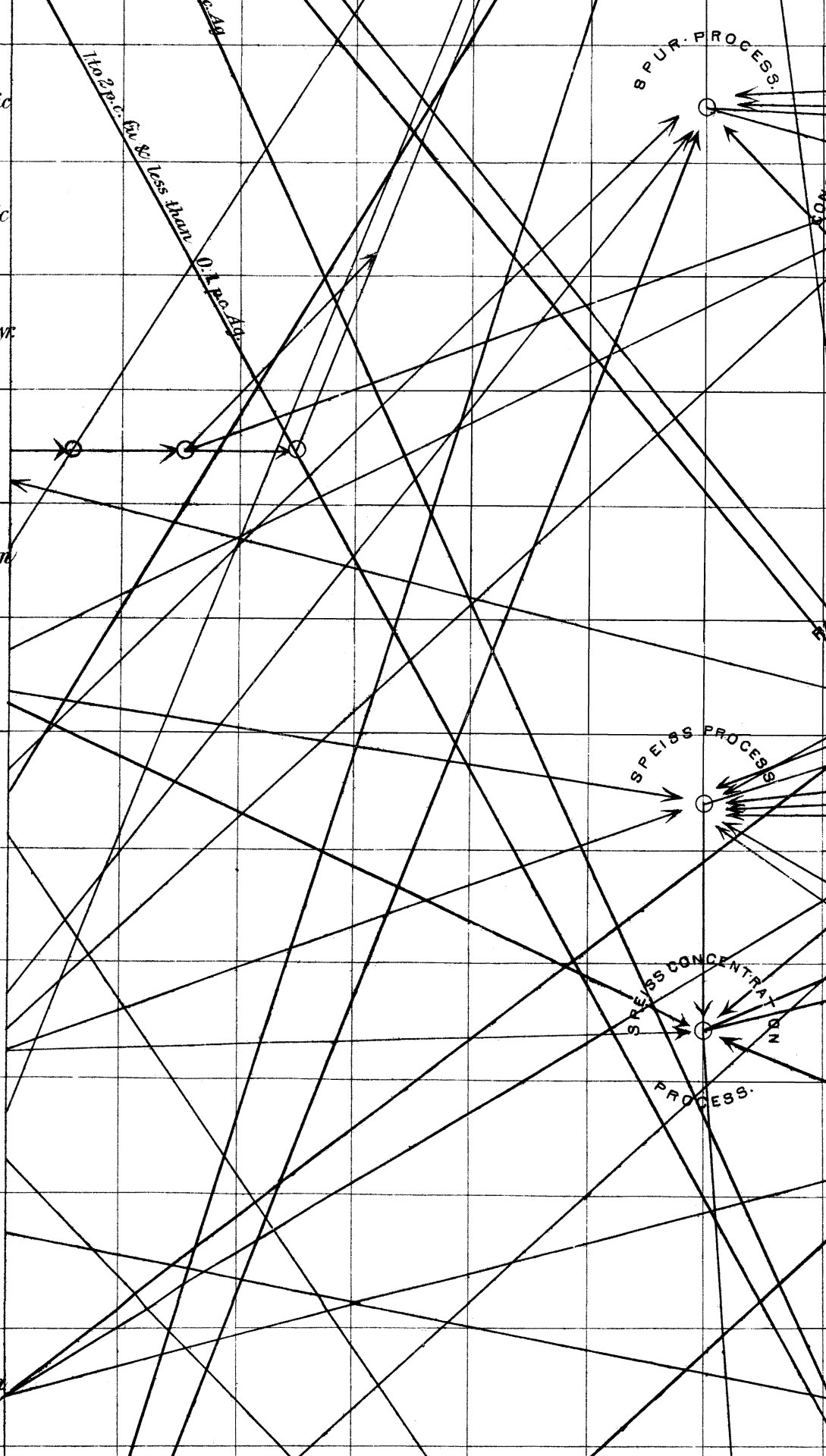
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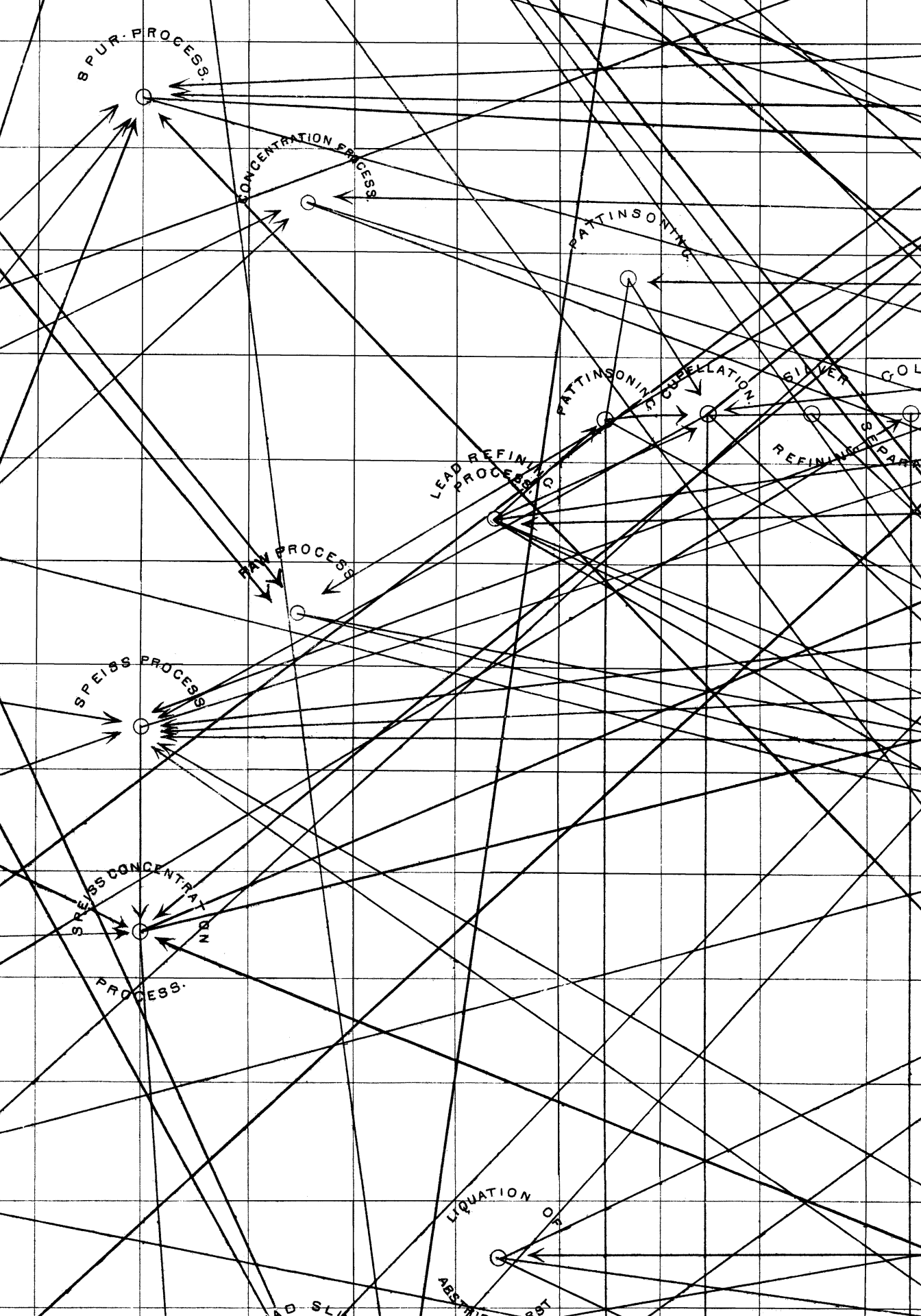
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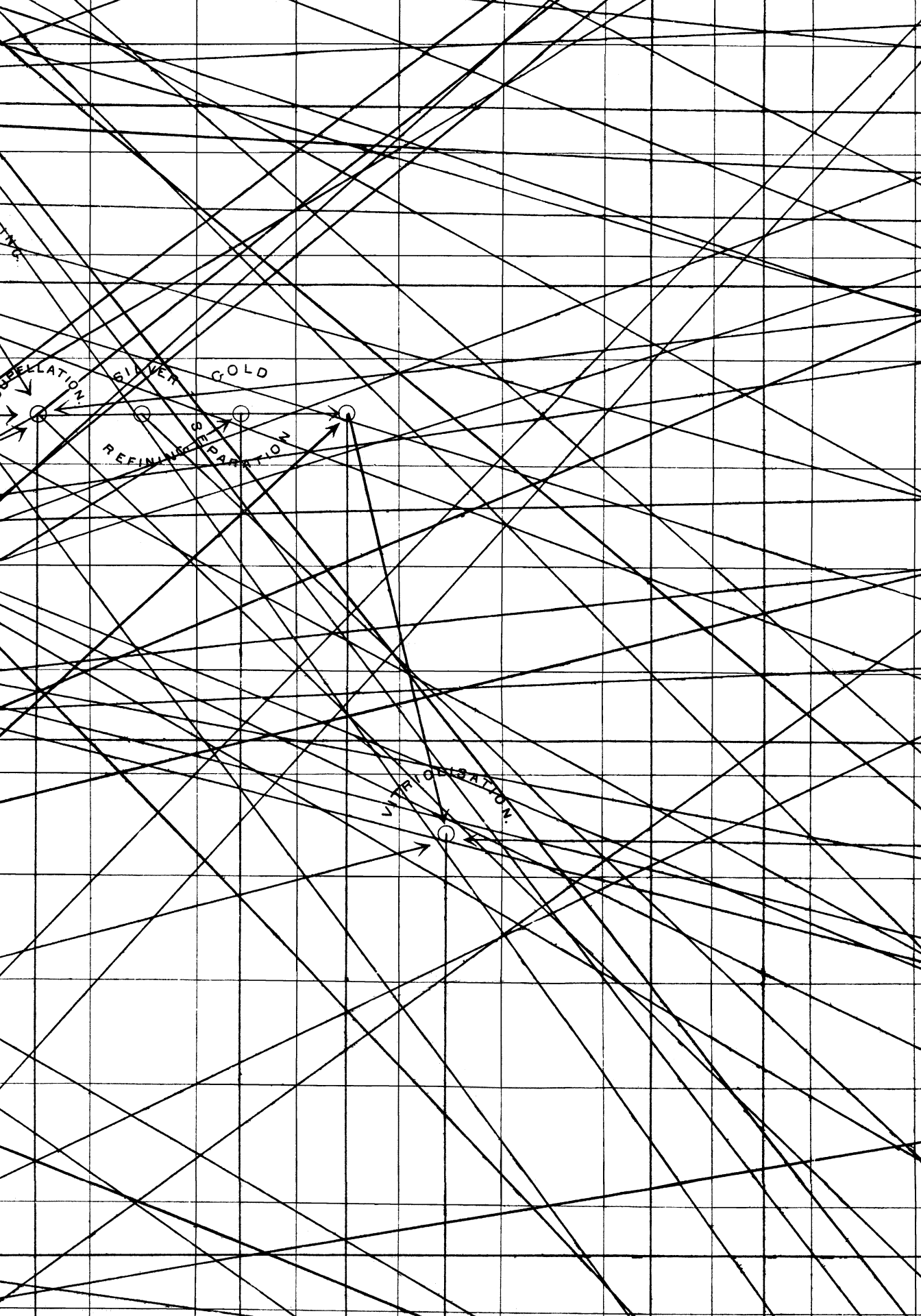
8 PUR. PROCESS.

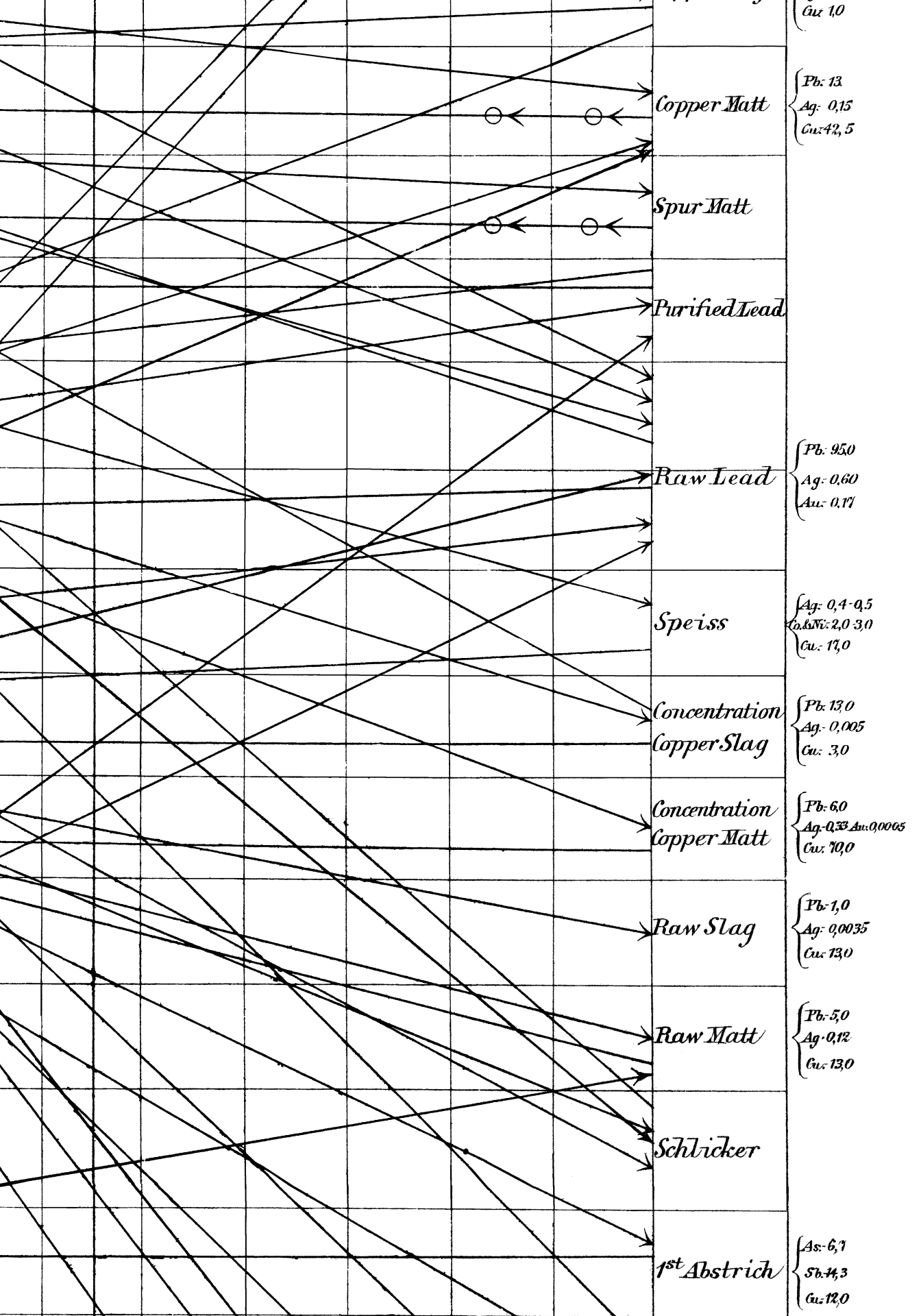
SPEISS PROCESS

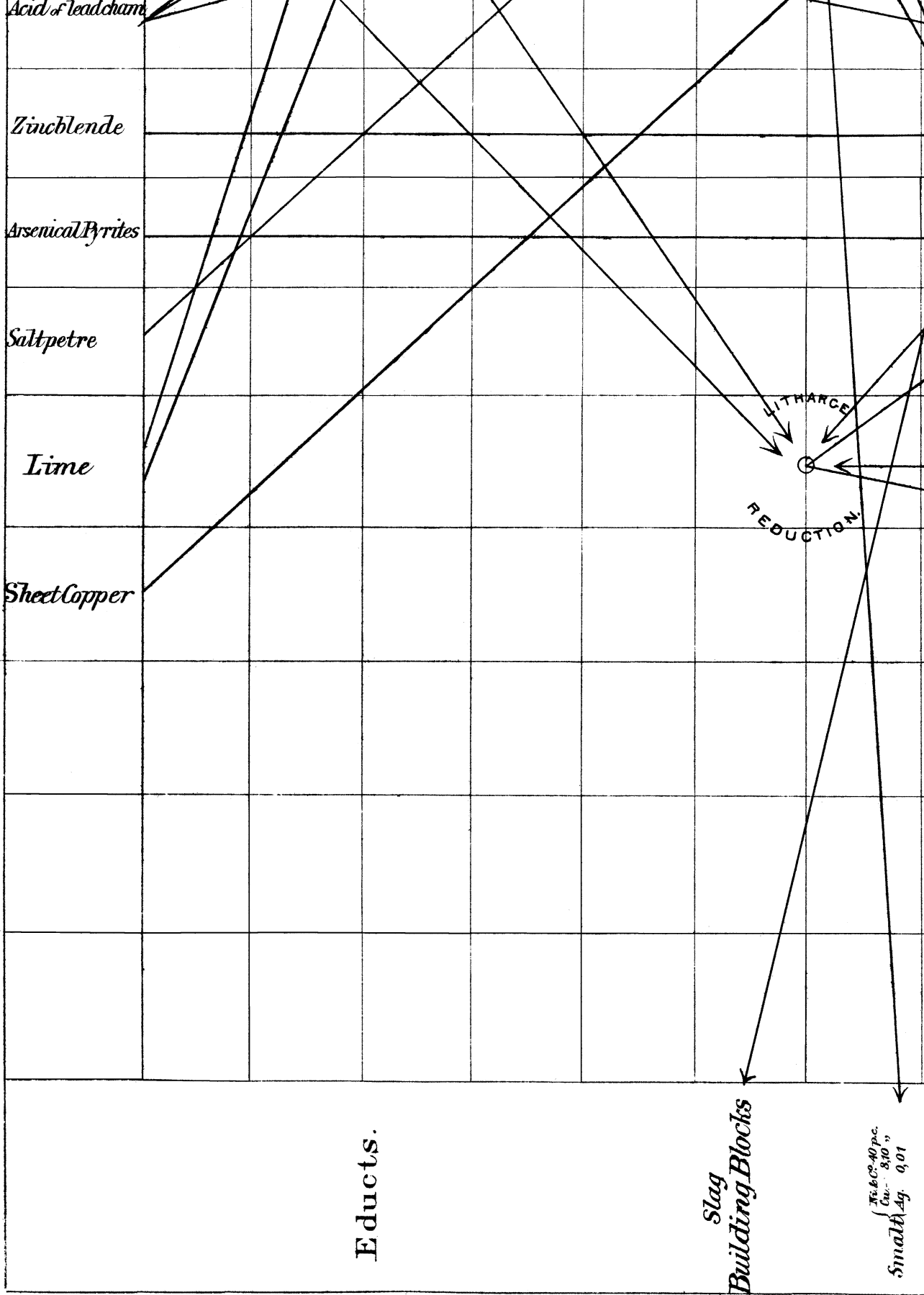
SPEISS CONCENTRATION PROCESS.



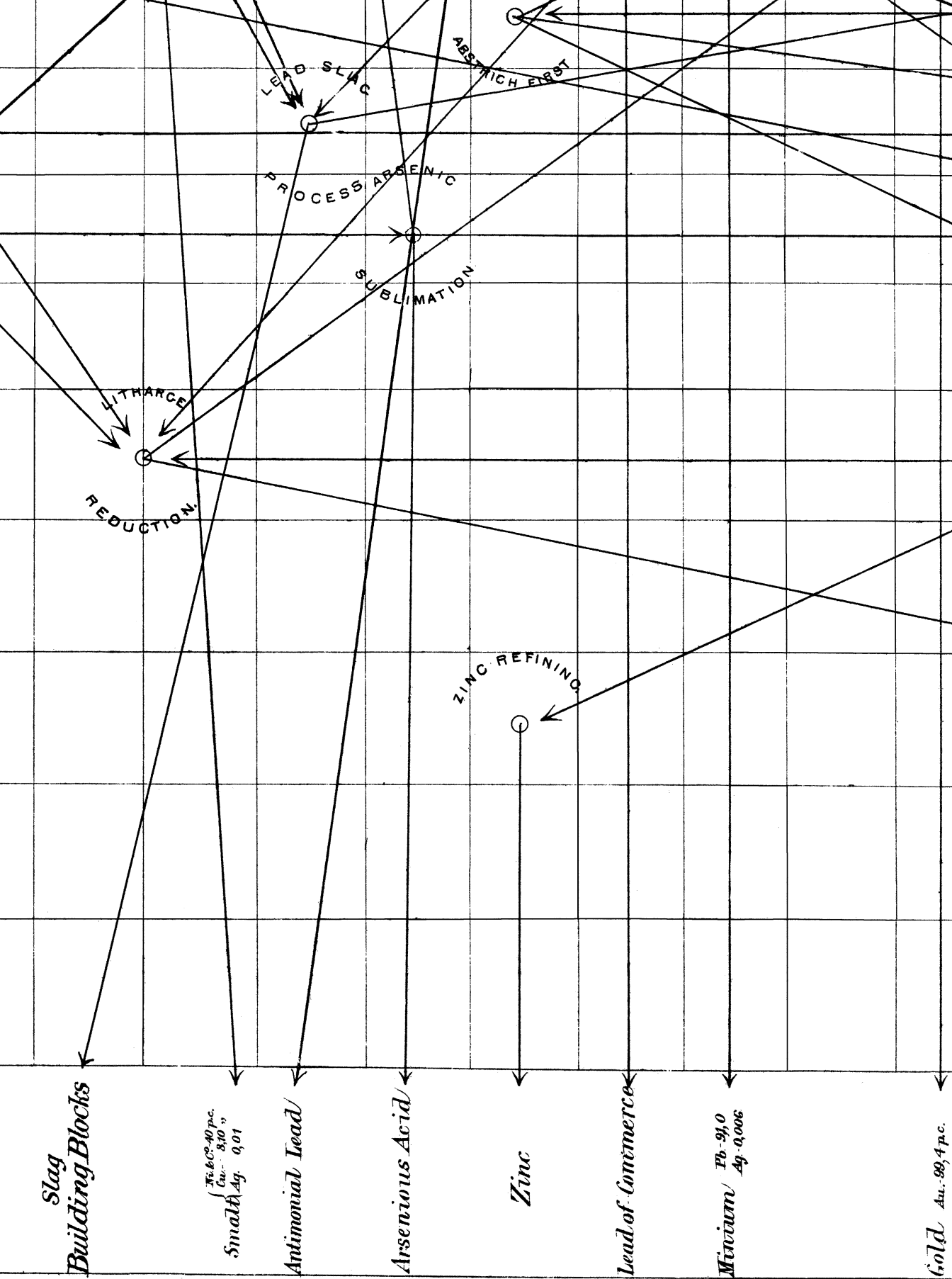




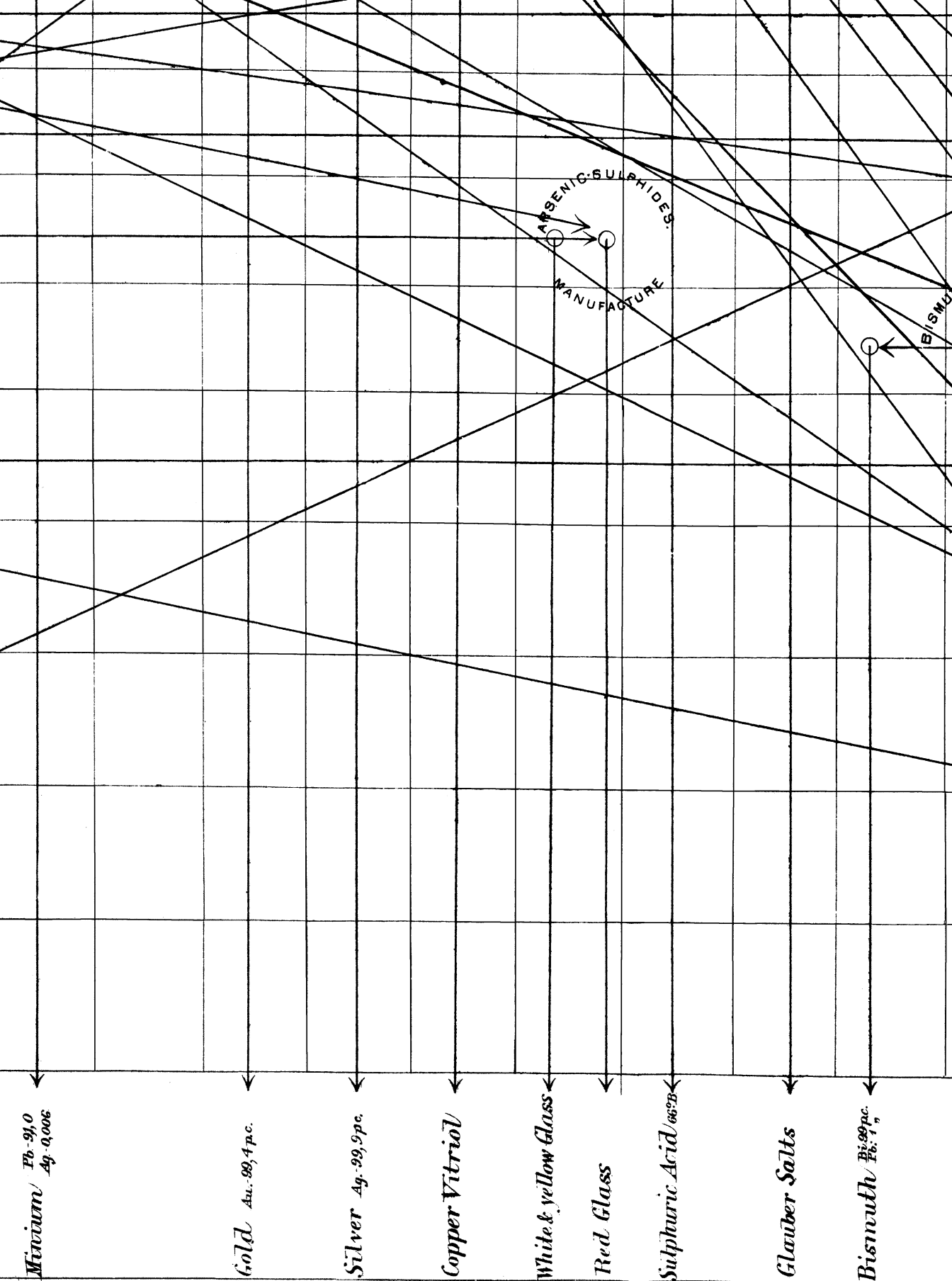




The arrow



The arrow heads point to the process by which a substance is treated, and are grouped
 The products of each process are given in the lines drawn out from
 Points on a line include the column on either side.



... is treated, and are grouped around the point indicating the process.
 ... in the lines drawn out from each centre.
 ... column on either side.

